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# EUROPEAN PATENT APPLICATION

21 Application number: 82101572.4

51 Int. Cl.<sup>3</sup>: G 02 B 1/08  
 C 08 G 69/32

22 Date of filing: 01.03.82

30 Priority: 02.03.81 US 238054

43 Date of publication of application:  
 20.10.82 Bulletin 82/42

64 Designated Contracting States:  
 DE FR GB

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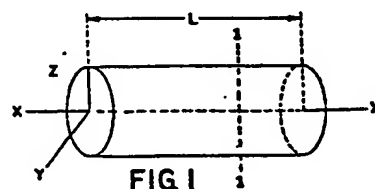
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54 Optical device including birefringent polymer.

57 Optical devices including a molecularly oriented highly birefringent polymer are disclosed. The devices include molecularly oriented polymers comprising recurring units (L) which exhibit a distribution of high electron density about the long axes (X) of the polymer and the recurring units (L) thereof. Transparent birefringent polymers comprising a plurality of recurring units (L) having a substantially cylindrical distribution of electron density about the long axis (X) of such units and the chain-extended polymers are included in optical devices and articles. The polymers exhibit high birefringence and simulate in a polymer the optical properties of a uniaxial crystal.



## Specification

## BACKGROUND OF THE INVENTION

1 This invention relates to an optical device or article. More particularly, it relates to such an article or device including a molecularly oriented highly birefringent poly-  
5 meric material.

Materials having a birefringent character have been variously applied in connection with the construction of filter and  
10 other optical devices. Frequently, a birefringent element utilized in an optical filter or other device will comprise a plate made from a monocrystalline form of birefringent material. Single crystals are expensive materials and are not readily formed to the desired shape or conformation required  
15 in particular applications. The size to which crystals can be grown represents an additional limitation on the utilization of such materials in optical devices.

Optical devices including a birefringent material in the  
20 form of a polymeric layer, such as may be formed by the unidirectional stretching of a suitable polymeric material, have also been described. Thus, light-polarizing devices utilizing a polymeric birefringent layer have been described in U.S. Patent 3,213,753 (issued October 26, 1965 to H.G. Rogers).  
25 Optical devices including polymeric birefringent materials have also been set forth, for example, in U.S. patent 3,506,333 (issued April 14, 1970 to E.H. Land) and in U.S. Patent 3,610,729 (issued October 15, 1971 to H.G. Rogers).  
Frequently, the efficiency of an optical filter, polarizing  
30 or other optical device including a birefringent element or layer will depend upon the realization of large net differences in refractive index between a birefringent material and adjacent or contiguous layers. In general, such net differences will be maximized where a birefringent material is  
35 highly birefringent. Correspondingly, large net differences in refraction indices of contiguous layers will be unattainable

- 1 where birefringent polymeric materials otherwise suited to  
application in an optical device tend to exhibit either low  
or only marginal birefringent character. Accordingly,  
optical devices including polymeric layers or elements ex-  
hibiting a highly birefringent character will be of  
5 particular interest for optical applications and enhanced  
efficiency.

#### SUMMARY OF THE INVENTION

- 10 The present invention provides an optical device or article  
which includes a molecularly oriented and optically uni-  
axial highly birefringent polymer. The polymer comprises  
repeating molecular units exhibiting high electron density  
substantially cylindrically distributed about the long axis  
15 of the polymer and the repeating units thereof. It has been  
found that the birefringent character of a polymer is  
importantly related to the molecular configuration or  
structure of the repeating units of the polymer and to the  
distribution of electron density about the long axis of the  
20 polymer and the repeating units thereof. Thus, it has been  
found that the provision, in a transparent polymeric  
material comprising a plurality of repeating units in  
chain-extended relationship, of a substantially cylindrical  
distribution of electron density about the long axis of the  
25 polymer permits the realization of high birefringence and  
the simulation in a polymeric material of optical  
properties of a uniaxial crystal.

- The present invention, thus, provides an optical device or  
30 article including a transparent molecularly oriented highly  
birefringent polymer, said highly birefringent polymer  
comprising repeating molecular units exhibiting high  
electron density substantially cylindrically distributed  
about the long axes of the polymer and the repeating units  
35 thereof, said highly birefringent polymer being optically



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1 uniaxial exhibiting only two indices of refraction. It has  
been found that birefringence of a polymeric material useful  
in articles or devices of the present invention exhibit bi-  
refringence in relation to the molecular configuration of the  
repeating molecular units and the cylindrical or ellipsoidal  
5 electron density distribution about the axes of the polymer  
and the recurring units thereof, said birefringence being  
in relation to said molecular configuration and said  
electron density distribution according to a dimensionless  
geometric index G represented by the relationship

$$G = 0.222 \times E \times \frac{L}{D}$$

where in E is a dimensionless eccentricity factor defined  
by the relationship

$$E = \frac{1 + e_L}{1 + e_T}$$

where  $e_L$  is the longitudinal eccentricity of the polarizability of the repeating molecular unit and  $e_T$  is the transverse eccentricity of the electron polarizability of the repeating molecular unit, L is the length of the repeating molecular unit along the main axis thereof and D is the mean diameter of the repeating molecular unit.

A preferred article of the present invention is a multi-layer light-transmitting device including at least one additional transparent layer having an index of refraction substantially matching one index of refraction of said layer of transparent molecularly oriented highly birefringent polymeric material and comprising isotropic or birefringent material; said at least one additional transparent layer, when a layer of birefringent material, having one index of refraction thereof substantially different from one index of refraction of said layer of transparent mole-

1 cularly oriented highly birefringent polymeric material and  
having a molecular orientation substantially perpendicular  
to the molecular orientation of said molecularly oriented  
highly birefringent polymeric material.

5

## THE DRAWINGS

Fig. 1 is a geometric representation of molecular di-  
mensions of a repeat unit of a polymeric material.

10 Fig. 2 is a cross-sectional view along the line 1-1 of  
Fig. 1.

Fig. 3 is a vectorial representation of bond and group  
polarizabilities of a repeat unit of a polymeric  
15 material.

Figs. 4a and 4b show, respectively, ellipsoidal and circular  
cross-sectional distribution of electron density  
about the long axis of a recurring unit of a  
20 polymeric material.

Fig. 5 is a diagrammatic fragmentary edge view of a  
light-transmitting device of the present invention  
illustrating the transmission of light rays  
25 therethrough.

Fig. 6 is a diagrammatic side view of an automotive  
vehicle headlamp which includes a light-polarizing  
filter of the invention.

30

Fig. 7 is a diagrammatic fragmentary edge view of another  
embodiment of the present invention showing in-  
cident light thereon being partly transmitted and  
partly reflected as separate linearly polarized  
35 components vibrating in orthogonal directions.

1 Fig. 8 is a diagrammatic side view of an optical beam-splitter device including a birefringent polymeric material.

# DETAILED DESCRIPTION OF THE INVENTION

5

As indicated hereinbefore, the present invention provides an optical device including a transparent, molecularly oriented and highly birefringent polymeric material. The birefringent polymeric material of the devices of the invention comprises repeat molecular units which exhibit high electron density substantially cylindrcally distributed about the long axes of the polymer and the repeat units thereof. The polymeric material, comprised of repeating units of molecular structure such as to provide a substantially cylindrical distribution of electron density about the long axis or backbone of the polymer, exhibits optical anisotropy or birefringence in accordance with the relationship

20 
$$G = 0.222 \left( \frac{1 + e_L}{1 + e_T} \right) \frac{L}{D}$$

where G represents the geometric index of a repeating unit;  $e_L$  is the longitudinal eccentricity of the electron polarizationability of the repeating molecular unit;  $e_T$  is the transverse eccentricity; L is the length of the repeating unit along the main axis thereof; and D is the mean diameter of the repeating molecular unit. The contribution to birefringence of the molecular structure of a repeating, chain-extending unit and of electron density distribution will be better understood by reference ot the drawings hereof.

In Fig. 1 is shown a geometrical representation of a repeating chain-extending molecular unit of a polymeric material. Each repeating unit may thus be visualized as a

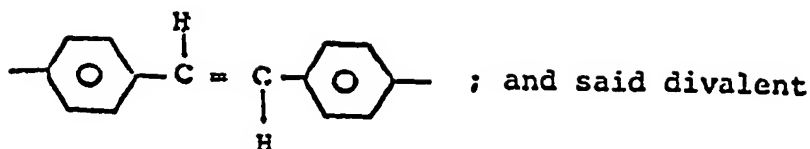
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1 repeating rod-like segment of finite length L and of a  
generally cylindrical configuration. Birefringence has been  
found to be importantly related to the molecular structure  
of the repeating units of the polymer in accordance with  
the relationship of geometric index G, set forth herein-  
5 before. A highly birefringent polymeric material useful in  
the optical devices hereof will thus comprise a plurality  
of molecular units in chain-extended relationship, each  
unit having a length L, shown in Fig. 1. The long axis X of  
each repeating unit forms, in the chain-extended polymer,  
10 the long axis or backbone. Each axis in Fig. 1 forms a  
right angle with respect to any other axis. The mean dia-  
meter D, set forth in the geometric index G, is determined  
for each repeating unit by the expression

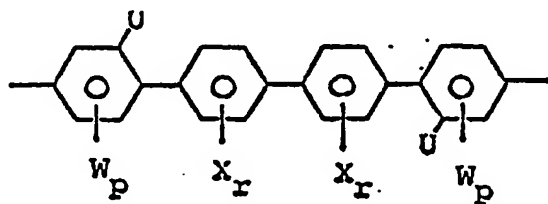
15  $D = \frac{Y + Z}{2}$ . In Fig. 2 is shown along line 1-1 of Fig. 1, a  
cross-sectional view. The shown Y and Z axes are at right  
angles to one another, the X axis comprising the axis of  
the cylinder extending in a direction normal to the plane  
of the paper.

20

In addition to a rigid rod-like geometry in a polymeric  
material as the result of an end-to-end combination of  
repeating units, the electron density distributed around  
the long axis of the polymer, variously treated as a  
25 cylindrical or ellipsoidal distribution, is believed to  
comprise a major contributing factor to optical anisotropy  
or birefringence. High electron density substantially  
cylindrically distributed around the long axis of a polymer  
is exhibited, for example, in a polymer of coaxially-bonded  
30 repeating units comprising non-coplanar, particularly  
orthogonal, biphenyl groups. An orthogonal relationship  
between adjacent phenylene rings can be nearly attained by  
the placement of substituents with large steric effects on  
at least one ortho-position of each ring, relative to the  
35 inter-ring bond. In Fig. 3 is shown a vectorial represent-



- 5 radical B is a substituted quaterphenylene radical having the formula



- 15 wherein each U is a substituent other than hydrogen, each W is hydrogen or a substituent other than hydrogen, each p is an integer from 1 to 3, each X is hydrogen or a substituent other than hydrogen and each r is an integer from 1 to 4, said U, W<sub>p</sub> and X<sub>r</sub> substitution being sufficient to provide said radical with a non-coplanar molecular configuration.

- 20 24. A device according to claims 22 or 23 each of U and X<sub>1</sub> in said formula of radical B is a substituent selected from the group consisting of halogen, nitro, alkoxy and trifluoromethyl.
- 25 25. A multilayer light-transmitting device comprising, in assembled bonded relation: a layer of transparent molecularly oriented highly birefringent polymer according to any of the preceding claims; said multilayer light-transmitting device including at least one additional transparent
- 30 layer having an index of refraction substantially matching one index of refraction of said layer of transparent molecularly oriented highly birefringent polymeric material and comprising isotropic or birefringent material; said at least one additional transparent layer, when a layer of
- 35 birefringent material, having one index of refraction

1 thereof substantially different from one index of refract-  
ion of said layer of transparent molecularly oriented  
highly birefringent polymer and having a molecular orient-  
ation substantially perpendicular to the molecular orient-  
ation of said molecularly oriented highly birefringent  
5 polymer.

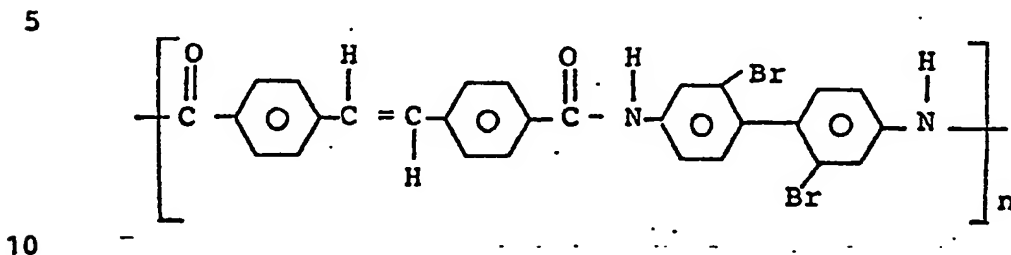
26. A multilayer light-transmitting device according to  
claim 25 wherein said layer of transparent molecularly  
oriented highly birefringent polymer is bonded to a trans-  
10 parent layer having an index of refraction substantially  
matching one index of refraction of said transparent  
molecularly oriented highly birefringent polymer.

27. A multilayer light-transmitting device according to  
15 claim 25 wherein said layer of transparent molecularly  
oriented highly birefringent polymer is bonded between two  
transparent layers, one transparent layer having an index  
of refraction substantially matching the lower index of  
refraction of said transparent molecularly oriented highly  
20 birefringent polymer.

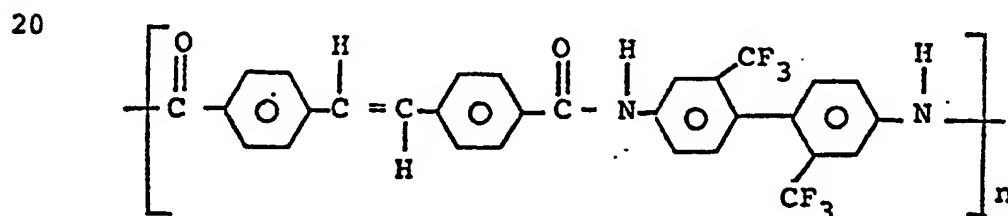
28. A multilayer light-transmitting device according to  
claim 27 wherein one of said two transparent layers has an  
index of refraction substantially matching the lower index  
25 of refraction of said transparent molecularly oriented  
highly birefringent polymeric material and the second of  
said two transparent layers has an index of refraction  
substantially matching the higher index of refraction of  
said transparent molecularly oriented highly birefringent  
30 polymer.

29. A multilayer light-transmitting device according to  
claim 25 comprising an alternating arrangement of a  
plurality of layers of said molecularly oriented highly  
35 birefringent polymer and a plurality of said additional

1 index value of 1.2 or higher. Experimentally determined  
 birefringence values for polymeric materials have been found  
 to correlate with calculated geometric indices. For example,  
 a geometric index of 1.20 was calculated for the recurring  
 structural unit of the following polymer:



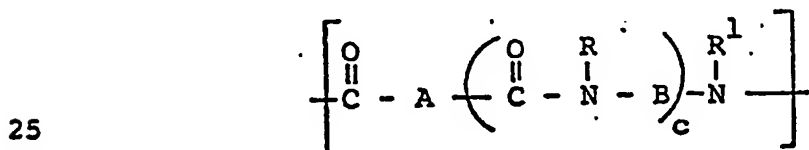
Theoretical maximum birefringence ( $\Delta n_{\max}$ ) was obtained by  
 plotting the orientation function for the polymer (calculated  
 from infrared dichroism) against the measured birefringence  
 15 of the polymer and extrapolating to 100 % orientation. A  
 $\Delta n_{\max}$  value of 1.20 was obtained. In like manner, a  
 correlation of geometric index G of 1.18 and  $\Delta n_{\max}$  of 0.98  
 was obtained in connection with the following polymer  
 comprising the shown recurring unit:



A number of polymeric materials comprising recurring units  
 having a geometric index as hereinbefore defined of about  
 0.5 or higher can be suitably employed in oriented form as  
 a birefringent polymeric material in an optical device of  
 30 the present invention. Rigid rod-like polymeric materials  
 comprised of recurring or repeating divalent units having  
 interbonded p-phenylene moieties of non-coplanar molecular  
 configuration are especially suited herein and are generally  
 characterized by geometric index values of one or greater  
 35 and by high birefringence. Exemplary of recurring units of

1 high geometric index G and high birefringence are certain  
 polyamide materials including recurring units comprised,  
 for example, of interbonded aromatic rings where the  
 aromatic rings are in twisted relation to one another, i.e.,  
 where the aromatic rings are in a non-coplanar molecular  
 5 configuration with respect to each other or, preferably, in  
 mutually orthogonal planes. It has been found that the  
 presence of substituent moieties on interbonded aromatic  
 radicals, of type and position such as to effect a non-  
 coplanar molecular configuration with respect to the inter-  
 10 bonded aromatic radicals, provides a recurring unit having  
 a high geometric index. The condition of non-coplanarity  
 among aromatic rings in a recurring unit, or presence in  
 such units of rings in "twisted" configuration relative to  
 one another has been found to be importantly related to  
 15 high birefringence in the rigid rod-like oriented polymers  
 resulting from the end-to-end joining of such recurring  
 units.

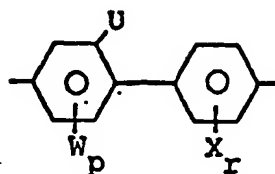
Among polyamide materials suited to application as highly  
 20 birefringent layers in the devices of the invention are  
 polyamides comprising repeating units of the formula



wherein each of A and B is a divalent radical, except that  
 B can additionally represent a single bond; R and R<sup>1</sup> are  
 30 each hydrogen, alkyl (e.g., methyl, ethyl), aryl (e.g.,  
 phenyl, naphthyl), alkaryl (e.g., tolyl), aralkyl (e.g.,  
 benzyl); c is zero or one; and wherein, when c is one, at  
 least one of A and B is a divalent radical selected from  
 the group consisting of:

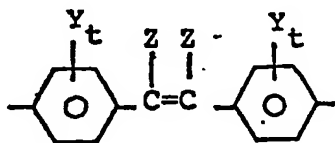


- 1 (1) a divalent substituted biphenyl radical



5  
 -- where U is a substituent other than hydrogen, each W is hydrogen or a substituent other than hydrogen, p is an integer from 1 to 3, each X is hydrogen or a sub-  
 10 stituent other than hydrogen and r is an integer from 1 to 4, said U, Wp and Xr substitution being sufficient to provide said radical with a non-coplanar molecular configuration; and

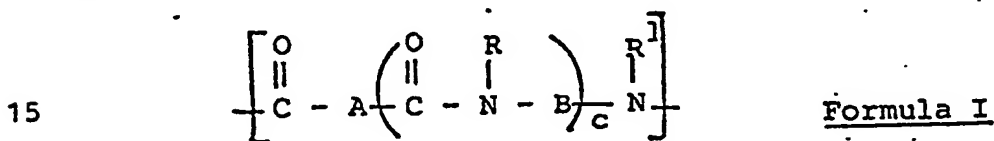
- 15 (2) a divalent substituted stilbene radical



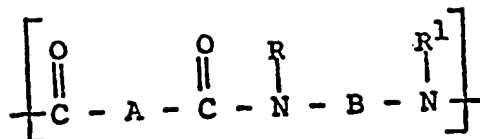
20  
 where each of Y and Z is hydrogen or a substituent other than hydrogen and each t is an integer from 1 to 4, with the proviso that when each said Z is  
 25 hydrogen, at least one said Y substituent is a substituent other than hydrogen positioned on the corresponding nucleus ortho with respect to the  
 30  $\begin{array}{c} Z \\ | \\ -C= \end{array}$  moiety of said radical, said Z and Y<sub>t</sub> substitution being sufficient to provide said radical with a non-coplanar molecular configuration;

and wherein, when c is zero, A is a divalent radical selected from the group consisting of radicals (1) and (2)  
 35 as hereinbefore defined.

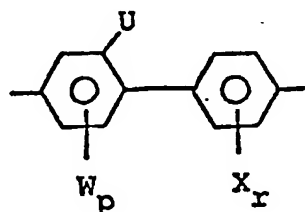
- 1 As used herein, substitution sufficient to provide a radical with a non-coplanar molecular configuration refers to substitution of type and position effective to confer to the interbonded aromatic radical thereof a non-coplanar molecular configuration such that the value of the geo-
- 5 metric index, as hereinbefore defined, is about 0.5 or higher. Preferably, the nature of such substitution will be sufficient to provide a G value of 1.0 or higher, and most preferably, 1.2 or higher.
- 10 As described hereinbefore, birefringent polyamides useful in devices of the present invention include those comprising recurring units of the formula



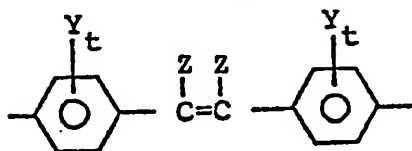
- wherein c is zero or one and wherein A (when c is zero) or at least one of A and B (when c is one) comprises a substituted divalent biphenyl radical or a sub-
- 20 stituted divalent stilbene radical. Thus, when c is zero, divalent radical A comprises a substituted biphenylene radical having a non-coplanar molecular configuration or a substituted divalent stilbene radical of non-coplanar molecular configuration. Similarly, when c is the integer one,
- 25 one or both of divalent radicals A and B comprises such substituted biphenylene or substituted stilbene radicals. It is preferred from the standpoint of ease of preparation that each of R and R<sup>1</sup> be hydrogen, although each of R and R<sup>1</sup> can be alkyl, aryl, alkaryl or aralkyl.
- 30 From inspection of the general formula set forth as descriptive of recurring units of the polyamides of Formula I, it will be appreciated that polyamides comprising the following recurring units are contemplated when c is one:

Formula II

5 In such recurring units, at least one of divalent radicals A and B will comprise a substituted biphenylene or substituted stilbene radical of non-coplanar, molecular configuration conforming to the formulae

Formula III

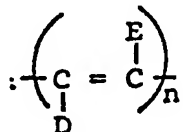
or

Formula IV

20 Where only one of said A and B radicals is a substituted biphenylene or substituted stilbene radical conforming to the radicals represented by the structures of Formulas III and IV, the remaining A or B radical can comprise any of a  
 25 variety of divalent radicals so long as the birefringent properties of the polyamide material are not effectively negated. In general, where only one of the A and B radicals conforms to the structures represented by Formulas III and IV, the remaining A or B radical will desirably be a  
 30 divalent radical which does not confer transverse eccentricity to the recurring unit. Similarly, where one of radicals A or B is a radical which confers transverse eccentricity to the recurring unit, the other of radical A or B will desirably be a radical which confers high long-  
 35 itudinal eccentricity such that the recurring unit of the

1 polymer exhibits a high geometric index. Suitable divalent radicals include, for example, unsubstituted biphenylene or stilbene radicals; phenylene; trans-vinylene; or ethynylene. Also suitable are polyunsaturated divalent radicals conforming to the formula

5



10 where n is an integer of at least two (e.g., two or three) and each of D and E is hydrogen or alkyl (e.g., methyl) and inclusive of such polyunsaturated divalent radicals as

trans-trans-1,4-butadienylene, i.e.,  $\begin{array}{c} \text{H} \quad \text{H} \\ | \quad | \\ \text{---C} = \text{C} - \text{C} = \text{C---} \\ | \quad | \\ \text{H} \quad \text{H} \end{array}$ ; and 1,4-

15

dimethyl-trans-trans-1,3-butadienylene, i.e.,  $\begin{array}{c} \text{CH}_3 \quad \text{H} \quad \text{H} \\ | \quad | \quad | \\ \text{---C} = \text{C} - \text{C} = \text{C---} \\ | \quad | \\ \text{CH}_3 \end{array}$

It will be appreciated that compounds containing amino groups directly attached to carbon atoms having linear unsaturated radicals are not stable and that, accordingly, the afore-

20 said vinylene, ethynylene and butadienylene radicals cannot serve as B radicals in the recurring units represented by the structure of Formula II.

25

In general, from the standpoint of maximized birefringent properties, it will be preferred that each of radicals A and B comprise a divalent radical exhibiting a non-coplanar molecular configuration and conforming to the structures

30 of Formulas III or IV. It will be appreciated, however, that the particular nature of such A and B radicals may affect the ability to readily orient the polyamide material, as by extrusion, stretching or the like. Accordingly, where the ability of a polyamide material to be oriented is

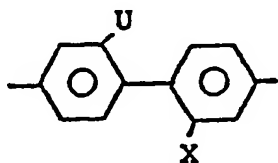
35 effectively reduced by the presence in the polyamide of

1 each of radicals A and B of non-coplanar molecular configuration and conforming to the structures of Formulas III or IV, it will be preferred that only one of such radicals A and B of the polyamide material conform to the structure of Formulas III or IV.

5

In the case of radicals A and/or B of the recurring type represented by Formula III, U will comprise a substituent other than hydrogen; W will be either hydrogen or a substituent other than hydrogen; and p will be an integer of  
10 from 1 to 3. In the case of such radicals, X will be hydrogen or a substituent other than hydrogen and r will be an integer of from 1 to 4. It will be appreciated from the nature of U, W, p, X and r, as set forth, that at least one aromatic nucleus of the biphenylene radical represented  
15 by Formula III will be substituted by a moiety other than hydrogen and that such substituent, U, will be positioned in an ortho relationship to the bridging carbon atoms of the biphenylene nuclei. Preferably, each aromatic nucleus of the biphenylene radical of Formula III will contain a  
20 substituent other than hydrogen positioned in an ortho relationship to the bridging carbon atoms of the biphenylene radical of Formula III and in this case, the divalent radical will have the following formula

25

Formula V

30 wherein each of U and X comprises a substituent other than hydrogen.

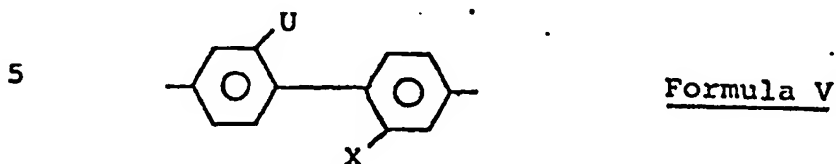
The nature and positioning of substituents U, W and X of the biphenylene radical of Formula III can vary widely,  
35 consistent with the provision of a biphenylene radical

- 16 -

1 having a non-coplanar molecular configuration. While  
applicants do not wish to be bound by precise theory or  
mechanism in explanation of the highly birefringent  
character observed in oriented polymers comprising recurring  
units of high geometric index, it is believed that the non-  
5 coplanar character conferred or promoted by the presence in  
a polymer of such recurring units provides a distribution  
of high electron density cylindrically about the long axis  
of the polymer. This distribution is believed to be  
importantly related to unusually high birefringence  
10 observed in such polymers.

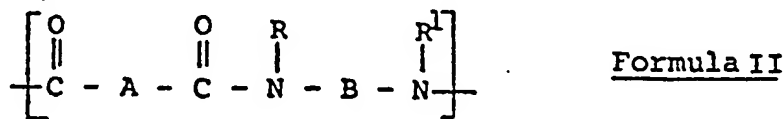
The nature of substituent U, Wp and Xr should be such as  
to provide the biphenylene radical of formula III with a  
non-coplanar molecular configuration referred to herein-  
15 before. Such configuration will in part be determined by  
the positioning and size of non-hydrogen substituents on the  
aromatic nuclei of the biphenylene radical and upon the  
number of such substituents on such aromatic nuclei. For  
example, where the biphenylene radical contains a single  
20 non-hydrogen substituent, i.e., substituent U, the nature  
and, in particular the size of such U substituent, should  
be such as to provide the desired non-coplanar molecular  
configuration. Suitable U substituents herein include  
halogen (e.g., fluoro, chloro, bromo, iodo); nitro; alkyl  
25 (e.g., methyl, ethyl); alkoxy (e.g., methoxy); substituted-  
alkyl (e.g., trifluoromethyl or hydroxymethyl); cyano;  
hydroxy; thioalkyl (e.g., thiomethyl); carboxy; sulfonic  
acid esters; sulfinic acid esters; carboxamide; sulfon-  
amide; amino; and carbonyl. Substituent X can comprise  
30 hydrogen or any of the substituents set forth in connection  
with substituent U. Preferably, at least one X substituent  
will comprise a substituent other than hydrogen. Each  
substituent W can comprise hydrogen or a substituent other  
than hydrogen as set forth in connection with substituents  
35 U and X. Normally, W will be hydrogen and p will be the  
integer 3.

- 1 Preferred polyamides herein are the polyamides comprising  
 recurring units having the biphenylene radical of  
 Formula V, i.e.,

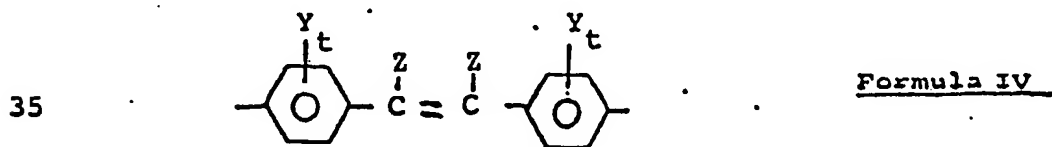


- wherein each of U and X is a substituent other than  
 10 hydrogen. The presence of such non-hydrogen substituents  
 on each of the aromatic nuclei of the radical promotes a  
 condition of non-coplanarity. Examples of such preferred  
 substituents, which may be the same or different, include  
 halo, nitro, alkoxy and substituted-alkyl (e.g., trifluoro-  
 15 methyl). While the presence of such non-hydrogen sub-  
 stituents is preferred from the standpoint of promoting  
 non-coplanarity, it will be appreciated, from the nature of  
 substituents W and X set forth in connection with Formula III  
 hereinbefore, that each X and W can be hydrogen and that,  
 20 accordingly, substituent U will in such instance desirably  
 comprise a bulky substituent such as will provide steric  
 hindrance to a condition of coplanarity.

- In the polyamides of the present invention which comprise  
 25 recurring units represented by the following formula



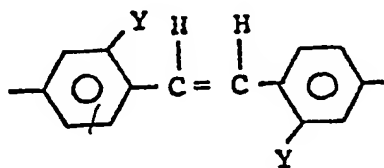
- 30 either or both of radicals A and B can comprise the sub-  
 stituted stilbene radical set forth hereinbefore as  
 Formula IV, i.e.,



1 In such stilbene radicals, the nature of each Y and Z will  
 be such as to provide the radical with a non-coplanar  
 molecular configuration. Preferably, non-coplanarity will  
 be provided by the presence of a single non-hydrogen sub-  
 5 stituent Z. Where each Z is hydrogen, non-coplanarity can  
 be provided by the positioning of a non-hydrogen Y sub-  
 stituent on at least one aromatic nucleus of the radical in

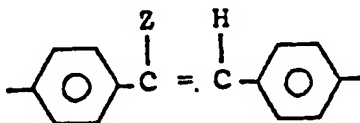
an ortho relationship to the  $\overset{\text{Z}}{\underset{|}{\text{C}}}=\text{}$  moiety of the radical.  
 Suitable non-hydrogen Y and Z substituents include, for  
 10 example, any of those set forth in connection with radicals  
 U, W and X defined hereinbefore.

Examples of preferred stilbene-type radicals included  
 within the class represented by Formula IV include the  
 15 following:



Formula VI

20 where at least one of the Y substituents is other than  
 hydrogen, preferably, halo or alkoxy; and

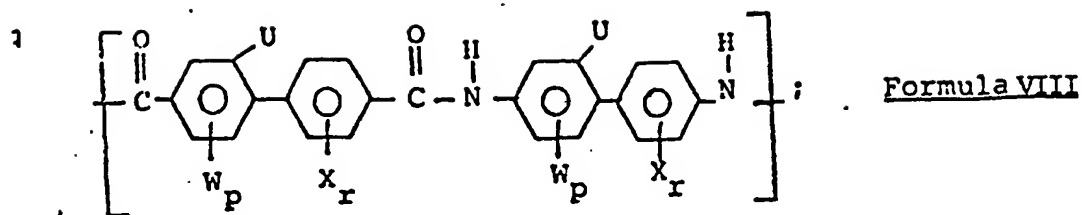


Formula VII

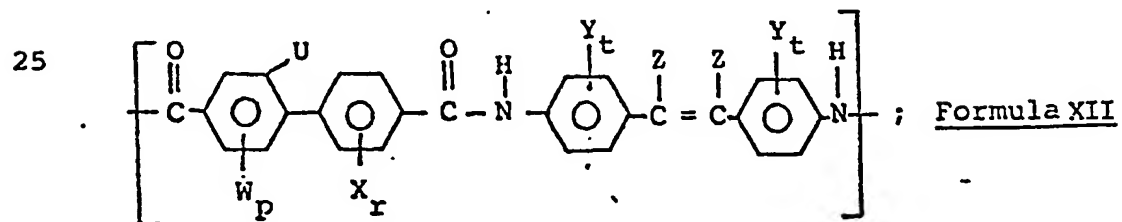
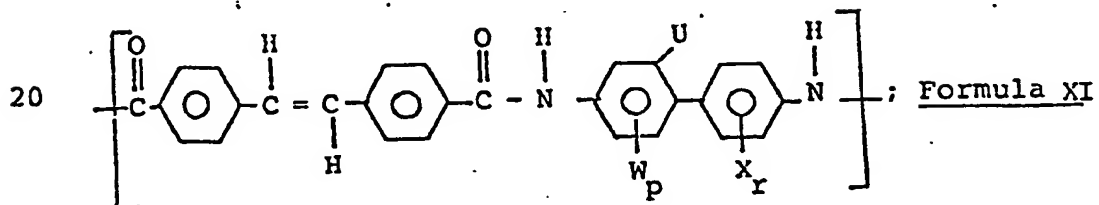
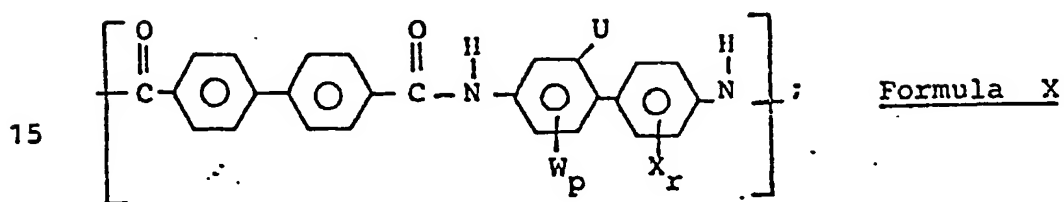
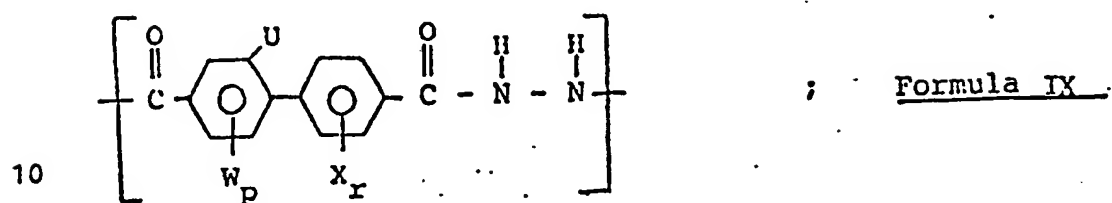
25 where Z is a substituent other than hydrogen, preferably  
 halo.

30 Inclusive of polyamides of the present invention represented  
 by the structure of Formula II are those having recurring  
 units represented by the following structures wherein,  
 unless otherwise specified, U, W, p, X, r, Y and t have  
 35 the meanings set forth hereinbefore:



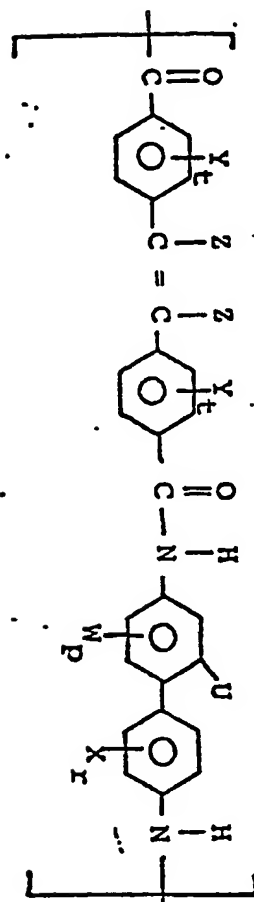


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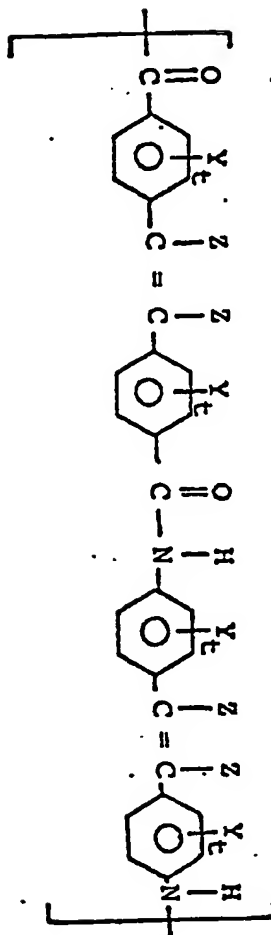


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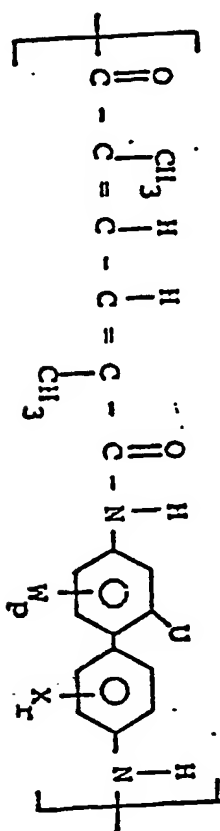
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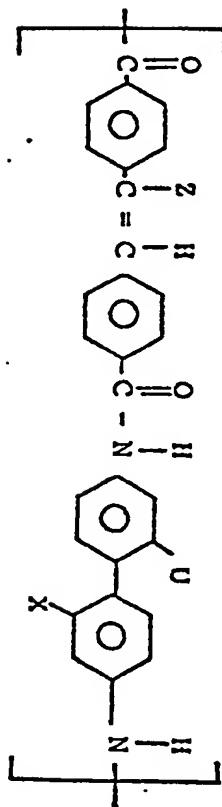
Formula XIII



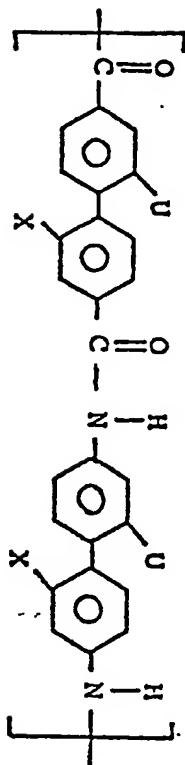
Formula XIV



Formula XV



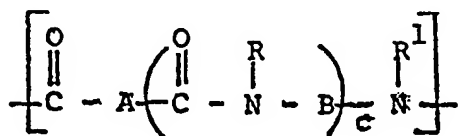
Formula XVI



Formula XVII

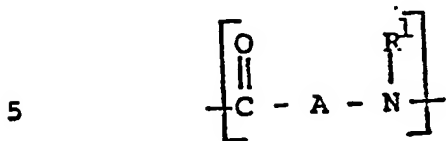
where each X is other than hydrogen.

From inspection of the general formula set forth as descriptive of recurring units of the polyamides, i.e. recurring units of the formula

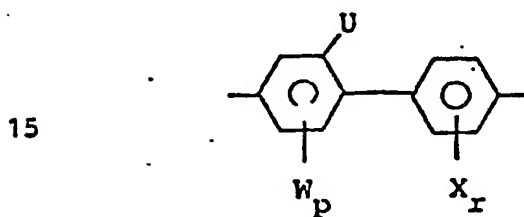


Formula I

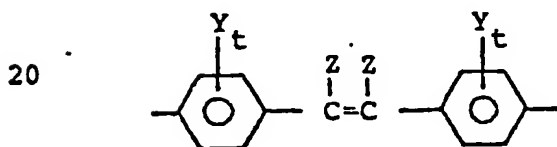
1 it will be appreciated that, when c is zero, the recurring units will be represented by the following formula:

Formula XVIII

In such recurring units, radical A will comprise a divalent radical having a non-coplanar molecular configuration and  
10 conforming to the structures of Formulas III and IV set forth hereinbefore, i.e.,

Formula III

or

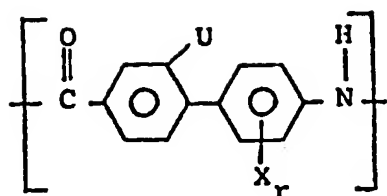
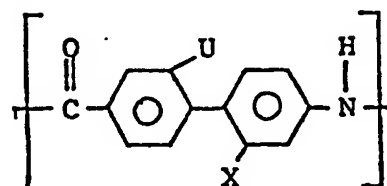
Formula IV

where U, W, p, X, r, Y, t and Z have the same meanings.

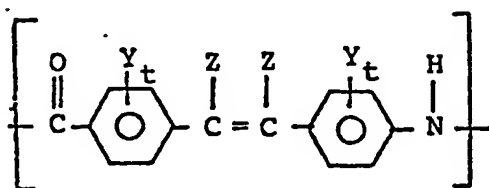
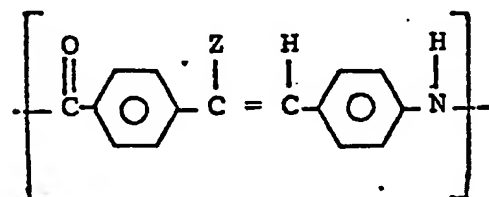
25

Inclusive of polyamides represented by the structure of Formula XVIII are those having recurring units represented

by the following structures wherein U, W, p, X, r, Y and t, unless otherwise indicated, have the meanings set  
30 forth hereinbefore:

; Formula XIX; Formula XX

where X is other than hydrogen;

; Formula XXI, Formula XXII

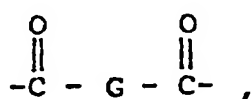
where Z is other than hydrogen.

While the polyamides described herein consist essentially of recurring units represented by the structures of Formulas II and XVIII, i.e., recurring units of the formulas

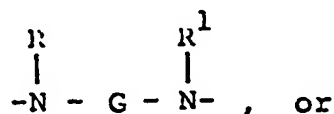


a combination of such recurring units, the polyamides can

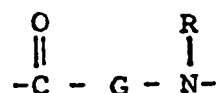
1 also comprise recurring units not conforming to the  
described structures of Formulas II and XVIII. Examples  
of recurring units which do not conform to such descriptions  
and which can be present in such polyamides in proportions  
which do not negate the high birefringence of the poly-  
5 meric material include, for example, recurring units having  
the formulas



Formula XXIII



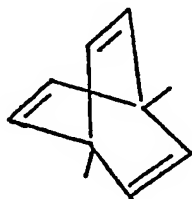
Formula XXIV



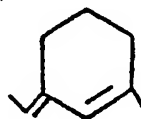
Formula XXV

wherein G is a divalent radical such as 1,4-phenylene;  
4,4'-biphenylene; vinylene; trans,trans-1,4-butadienylene;  
4,4'-stilbene; ethynylene; 1,5-naphthalene; 1,4-dimethyl-  
20 trans,trans-1,4-butadienylene; 2,4'-trans-vinylphenylene;  
trans,trans-4,4'-bicyclohexylene; 2,5,7-bicyclooctatriene-  
1,4-,

i.e.,



; or



30

Other divalent radicals can, however, serve as radical G  
provided that such radicals do not adversely and materially  
reduce the birefringence of the polyamide material. It will  
be appreciated that G cannot represent an aliphatic un-  
35 saturated moiety where a carbon atom thereof having such  
unsaturation is to be bonded to an amino group.

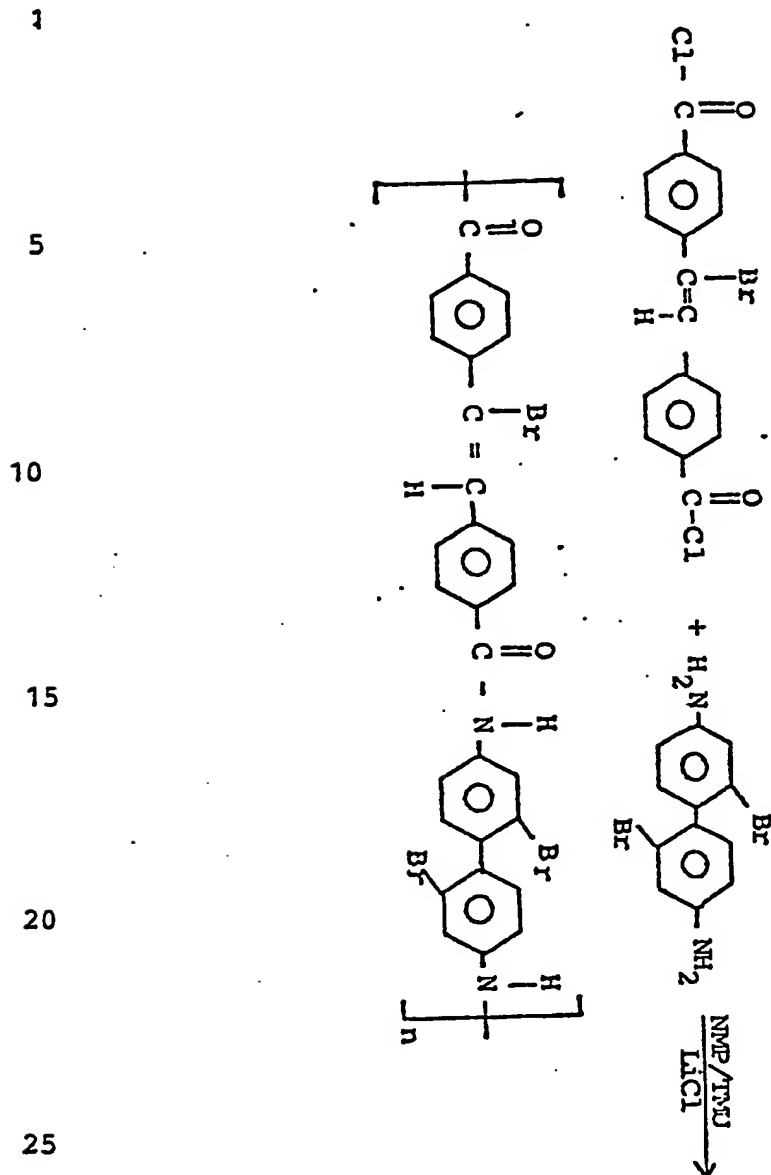
1 The substituted polyamides utilized in devices of the  
 present invention can be prepared by resort to polyamide  
 synthesis routes involving the polymerization of suitable  
 acid halide and amine monomers in an organic solvent which  
 may contain a solubilizing agent such as lithium chloride  
 5 or chain-terminating agent where desired. Polyamides of  
 the type represented by the structure of Formula I can be  
 prepared, for example, by the reaction of a dicarboxylic acid halide

of the formula  $\text{Hal}-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-\text{A}-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-\text{Hal}$  with a diamine of the formula  
 10  $\text{H}-\overset{\text{R}}{\underset{\text{R}^1}{\text{N}}}-\text{B}-\overset{\text{R}}{\underset{\text{R}^1}{\text{N}}}-\text{H}$ , where Hal represents halogen, such as chloro or  
 bromo and A and B have the meanings hereinbefore set forth,  
 except that B cannot represent an aliphatic unsaturated  
 moiety. The reaction can be conducted in an organic solvent  
 15 such as N-methyl pyrrolidone (NMP), tetramethylurea (TMU)  
 or a mixture thereof, and preferably, in the presence of  
 a salt such as lithium chloride to assist in the solubiliz-  
 ation of reactant monomers and maintenance of a fluid  
 reaction mixture. The preparation of a polyamide of the  
 20 present invention can be illustrated by reference to the  
 preparation of poly(2,2'-dibromo-4,4'-biphenylene)-trans-  
 $\alpha$ -bromo-p,p'-stilbene dicarboxamide, a preferred polyamide  
 herein, in accordance with the following reaction scheme:

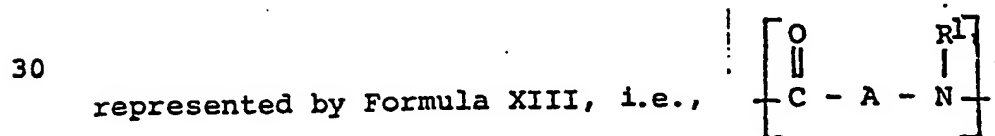
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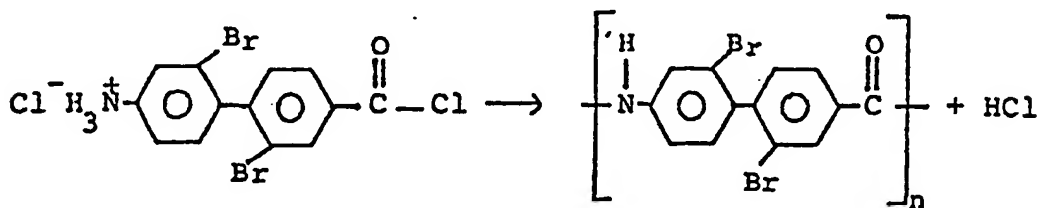
Polyamides containing recurring units having the structure



can be prepared, for example, by the polymerization of a  
 p-amino-aryl halide monomer in the form of a halide,  
 35 arylsulfonate, alkylsulfonate, acid sulfonate, sulfate or



1 other salt. This polymerization can be illustrated by  
 reference to the preparation of poly(2,2'-dibromo-4,4'-  
 biphenylene)carboxamide in accordance with the following  
 reaction scheme showing the polymerization of the hydro-  
 chloride salt of 2,2'-dibromo-4-amino-4'-chlorocarbonyl-  
 5 biphenyl:



Substituted polyamides useful in optical devices of the  
 present invention can be prepared by polymerization of  
 15 correspondingly substituted monomers in a suitable organic  
 reaction solvent. Such solvents include amide and urea  
 solvents including N-methyl-pyrrolidone and N,N,N',N'-tetra-  
 methylurea. Other suitable reaction solvent materials  
 include N-methyl-piperidone-2; N,N-dimethylpropionamide;  
 20 N-methylcaprolactam; N,N-dimethylacetamide; hexamethyl-  
 phosphoramidate; and N,N'-dimethylethylene urea. The poly-  
 merization can be conducted by dissolving the monomer or  
 monomers to be polymerized in the reaction solvent and  
 allowing the exothermic polymerization reaction to occur  
 25 usually with the aid of external cooling. In general, the  
 polymerization will be conducted initially at a temperature  
 of from about -20°C to about 15°C, and preferably, in the  
 range of from about -5°C to about 5°C. Thereafter,  
 usually within about one-half hour to one hour, the  
 30 reaction will be heated with formation of a thickened poly-  
 meric mass of gel-like consistency. In general, the poly-  
 merization reaction will be conducted over a period of from  
 about 1 to 24 hours, preferably about 3 to 18 hours.

35 While the monomer or monomers to be polymerized can be

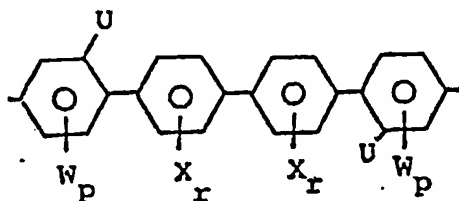
1 dissolved in a suitable amide or urea solvent and allowed  
to react with formation of the desired polymeric material,  
a preferred reaction sequence where a mixture of copoly-  
merizable monomers is utilized involves the preparation  
of a solution of a first monomer in the amide or urea  
5 solvent and the addition thereto of a second or other  
monomer or a solution thereof in a suitable organic  
solvent therefor, such as tetrahydrofuran. External cooling  
of the resulting reaction mixture provides the desired  
polyamide material in high molecular weight and minimizes  
10 the production of undesired side reactions or by-products.

The polyamide materials prepared as described can be  
recovered by combining the polymerization reaction mixture  
with a non-solvent for the polymer and separating the poly-  
15 mer, as by filtration. This can be effectively accomplished  
by blending the polymerization mixture with water and  
filtering the solid polyamide material. The polyamide can  
be washed with an organic solvent such as acetone or ether  
and dried, for example, in a vacuum oven.

20 Polyamide materials as described hereinbefore and methods  
for their preparation are described in greater detail in  
the European Patent Application of H.G. Rogers, R.A.  
Gaudiana, J.S. Manello and R.A. Sahatjian, Attorney  
25 Docket No. 3920-X-11.692 filed of even date herewith.

While the transparent highly birefringent materials useful  
in the devices of the present invention have been set forth  
by reference to certain polyamides, represented by the  
30 structures of Formulas II and XVIII, it will be appreciated  
that transparent highly birefringent polymeric materials  
of other polyamide types, or of types or classes other than  
polyamides, can likewise be utilized herein where the  
repeating units of such polymers have a substantially  
35 cylindrical distribution of electron density about the  
long axis of the polymer.

1 Particularly useful herein are transparent polyamide  
materials comprising recurring units corresponding to  
Formula I hereof wherein c is zero or one, each of A and  
B is a divalent radical, except that B can additionally  
represent a single bond, and at least one of A and B is  
5 a substituted-quaterphenylene radical having the formula



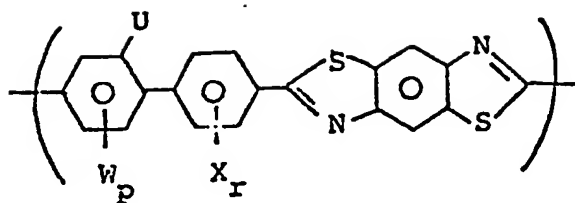
10

wherein U, W, X, p and r have the meanings set forth  
herein and the U, W<sub>p</sub> and X<sub>r</sub> substitution is sufficient to  
15 provide the radical with a non-coplanar molecular con-  
figuration.

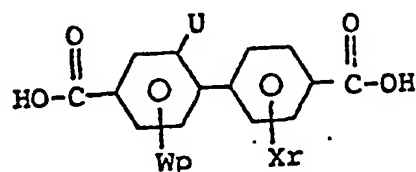
The above substituted-quaterphenylene polyamides can be  
prepared, for example, by reaction of a suitably sub-  
20 stituted quaterphenylene diamine and a dicarboxylic acid  
or halide. These polymers and their preparation are  
described in greater detail and are claimed in the  
European Patent Application of R.A. Gaudiana and P.S.  
Kalyanaraman, (Attorney Docket No. 3920-X-11.692) filed of  
25 even date herewith.

Transparent polymeric materials from classes other than  
polyamides and which can be utilized herein include, for  
example, polymers having thiazole, imidazole, oxazole  
30 and/or ester linkages. For example, polymeric materials  
comprising the following thiazole-containing recurring  
units, where U, W, X, p and r have the meanings herein-  
before ascribed, can be utilized herein:

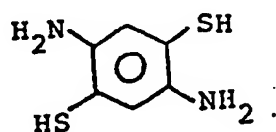
- 30 -



5 Such polymeric materials can be prepared by reaction of a dicarboxylic acid compound of the formula

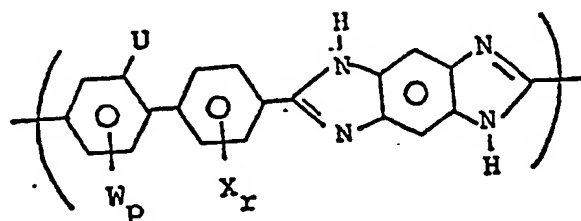


with an amino-thiol of the formula



20 in a suitable organic solvent with recovery of the desired polymeric material.

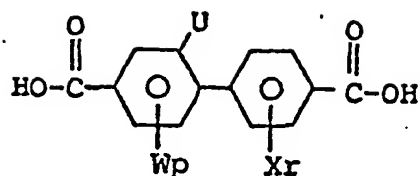
Polymers comprising the following imidazole-containing repeating units can also be employed herein, where U, W, X, p and r have the meanings hereinbefore described.



These polymers can be prepared, for example, by reaction of a dicarboxylic acid compound of the formula

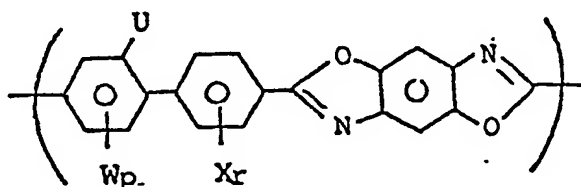
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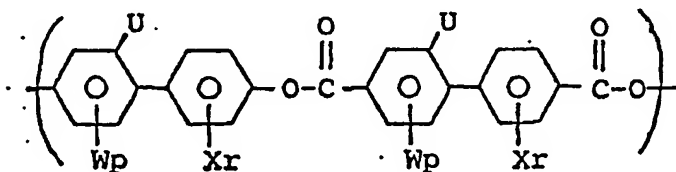


5 with 1,2,4,5-tetramino-benzene.

Polymers containing recurring units having an oxazole moiety can be suitably prepared by reaction of a dicarboxylic acid compound as aforescribed with, for example, 1,4-dihydroxy-2,5-diamino-benzene, with formation of a polymer containing the following recurring units where U, W, X, p and r have the meaning set forth hereinbefore.



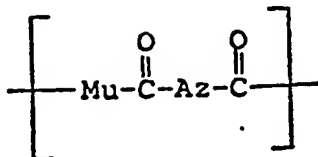
Polyester materials can also be suitably employed herein. Exemplary of such polyesters are those having recurring units of the formula



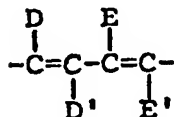
wherein each U, W, X, p and r has the meaning set forth hereinbefore.

Other polymers that can be utilized in optical devices of the present invention are polymers comprising recurring units of the formula

1



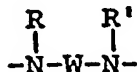
5 where Mu is a divalent radical having the formula



10

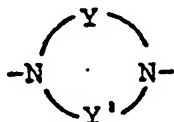
where each of D, D', E and E' is hydrogen, alkyl or substituted-alkyl; and Az is a divalent radical having the formula

15



where each of R and R' is hydrogen, alkyl, aryl, alkaryl or aralkyl and W is a single bond, alkylene or alkenylene; or Az is a divalent radical having the formula

20



25 where each of Y and Y' represent the atoms necessary to complete with the nitrogen atoms to which they are bonded a piperazine or substituted-piperazine radical.

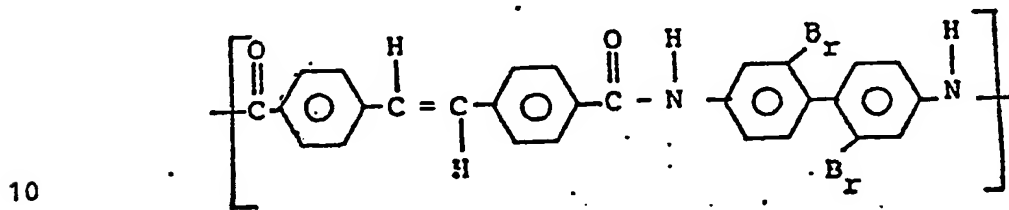
30 These polymers can be conveniently prepared by reaction of a dienonic acid chloride such as mucononic acid chloride or  $\alpha, \alpha'$ -dimethylmuconic acid chloride with hydrazine or a diamine such as piperazine, 2-methylpiperazine or 2,5-dimethylpiperazine.

35 The polymeric materials utilized in the devices of

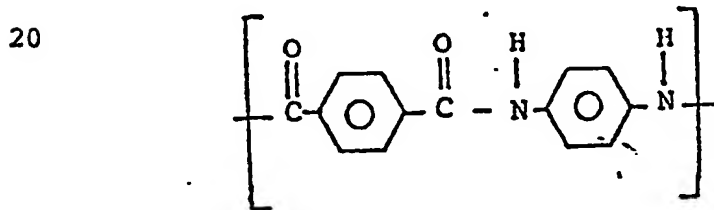
1 the present invention can be variously formed or shaped  
into films, sheets, coatings, layers, fibrils, fibres or  
the like. For example, a solution of a substituted poly-  
amide as described hereinbefore, in a solvent material such  
as N,N-dimethyl-acetamide, optionally containing lithium  
5 chloride solubilizing agent, can be readily cast onto a  
suitable support material for the formation of a polymeric  
film or layer of the polyamide material. The polymeric film  
can be utilized for the production of a birefringent poly-  
meric film or sheet material which can be utilized in an  
10 optical device of the invention. Thus, a polymeric film or  
sheet material can be subjected to stretching so as to  
introduce molecular orientation and provide a film material  
having a highly birefringent character.

15 Known shaping or forming methods can be utilized for the  
orientation of polymeric materials suited to application  
in devices of the present invention. Preferably, this will  
be accomplished by unidirectional stretching of a poly-  
meric film, by extrusion of the polymer into a sheet,  
20 layer or other stretched form, or by the combined effects  
of extrusion and stretching. In their oriented state, the  
polymers utilized herein exhibit unusually high bire-  
fringence. In general, greater birefringence will be ob-  
served in the case of polymeric materials exhibiting a  
25 greater degree of molecular orientation. It will be  
appreciated, however, as has been pointed out hereinbefore,  
that the particular molecular structure or configuration of  
the polymeric material may affect desired physical  
attributes of the polymer material or otherwise impose a  
30 practical limitation upon the degree of orientation that  
can be realized by stretching or other means. It is a  
significant aspect of the present invention, however, that  
the polymeric birefringent materials utilized in the  
devices of the present invention, particularly for a given  
35 degree of orientation, exhibit unusually high birefringence.

1 In this connection, it is to be noted, for example, that  
 the substituted polyamides described herein will often ex-  
 hibit higher birefringence than the more highly oriented  
 materials of different polymeric structure. For example,  
 an extruded film of a substituted polyamide hereof  
 5 comprised of recurring units of the formula



and having a degree of orientation in the range of from  
 about 80 % to 85 % as determined from infra-red dichroism,  
 15 exhibited a birefringence ( $\Delta n$ ) of 0.865 as measured  
 utilizing principles of interferometry. In contrast, a  
 polyamide fibre material and comprised of recurring units  
 of the formula:



25 is reported in the literature, A.A. Hamza and J. Sikorski,  
 J. Microscopy, 113, 15 (1978), as having a birefringence  
 of 0.761, as measured by interferometric technique and at a  
 degree of orientation of about 90 % to 95 %.

30 The birefringent polymers useful in the devices hereof will  
 desirably simulate to the maximum practical extent the  
 optical properties of a uniaxial crystal. Accordingly, the  
 birefringent polymers will exhibit substantially uniaxial  
 35 optical behaviour, i.e., only two indices of refraction.



- 1 Optical efficiency and maximum birefringence will be realized where such substantially uniaxial behaviour is exhibited by such polymers.

The molecularly oriented birefringent polymers utilized  
5 herein will preferably exhibit a birefringence of at least about 0.2, and more desirably, a birefringence of at least 0.4. Thus, preferred polymers for use in the articles hereof will exhibit substantially uniaxial optical behaviour and a birefringence of at least about 0.2 and will be  
10 comprised of recurring units having a geometric index of about 0.5 or higher.

The birefringent polymeric materials utilized in the devices of the present invention, in addition to exhibit-  
15 ing high birefringent properties, are advantageous from the standpoint of their transparency. In contrast to polymeric materials which become decidedly opaque as a result of stretching, birefringent materials hereof exhibit transparency in unoriented and stretched forms. For example,  
20 the substituted polyamides described herein exhibit a high transparency and a low order of light scattering, exhibiting a ratio of amorphous to crystalline material of from about 10:1 to about 20:1 by weight. These materials are, thus, suited to optical applications where a light-trans-  
25 missive, highly refractive and birefringent material is desirably utilized. Depending upon the nature of substituent moieties on the divalent radicals of the recurring units of these polyamides, colourless or nearly colourless polymeric films or layers can be fabricated.  
30 Where, for example, nitro-substituted biphenylene radicals are present, a yellow transparent film or fibre can be fabricated. Films, coated or other shaped forms of the substituted polyamides can be redissolved and reshaped or refabricated if desired. Depending upon the nature of  
35 particular recurring units of the polyamide materials,

1 and particularly the nature of substituent moieties and solvent materials, the solubility characteristics of these substituted polyamides can be varied or controlled to suit particular applications.

5 The birefringent properties of polymers utilized in the devices of the present invention can be determined by the measurement of physical and optical parameters in accordance with known principles of physics and optics. Thus, for example, the birefringence ( $\Delta n$ ) of a suitable birefringent polymeric material can be determined by the  
10 measurement of optical phase retardation (R) and film thickness (d) and calculation of birefringence in accordance with the relationship

$$15 \quad \Delta n = \frac{R \lambda}{d}$$

where  $\lambda$  represents the wavelength of light utilized for the conduct of the measurements. Alternatively, parallel refractive index and perpendicular refractive index of the  
20 film material can be measured utilizing Becke line analysis or critical angle measurement.

A preferred method for determining the birefringence of useful polymeric materials involves the measurement of  
25 retardation of the polymeric material by a method utilizing principles of polarized-light microscopy and interferometry. Such method provides desired precision and accuracy in the measurement of the phase difference between a sample ray passing through a sample of polymeric material and a  
30 reference ray passing through a neighbouring empty area (embedding medium or air) of the same thickness. The light emitted by a low-voltage lamp of a microscope is linearly polarized by passage through a polarizer and, in turn, is passed through a condenser, a calcite plate beam  
35 splitter, a half-wave retarder plate, the polymeric sample,

1 a beam recombinator calcite plate, and through an  
analyzer whose transmission direction is vertical to that  
of the polarizer (crossed position). In the analyzer the  
components vibrating in its absorption direction are ex-  
tinguished, whereas the components of both rays in the  
5 transmission direction are transmitted and interfere. The  
phase difference between sample and reference beams, caused  
by the molecular structure or configuration of the poly-  
meric sample, is measured with compensators. From these  
measurements, the thickness and refractive index of the  
10 polymeric material can be determined. By determining index  
of refraction of the polymeric sample for both parallel and  
perpendicular directions, birefringence can, by difference,  
be determined. A suitable method and apparatus for deter-  
mining phase retardation, index of refraction and bire-  
15 fringence for the polymeric materials utilized herein is  
a pol-interference device according to Jamin-Lebedeff  
described in greater detail by W.J. Patzelt, "Polarized-  
light Microscopy," Ernst Leitz GmbH, Wetzlar, West Germany,  
1974, page 92.

20

Preferred optical devices of the present invention are  
multilayer devices which include a layer of molecularly  
oriented and highly birefringent polymeric material as  
described hereinbefore, and in addition, at least one  
25 layer of isotropic or birefringent material. The additional  
layer or layers whether isotropic or birefringent,  
comprises a material having an index of refraction matching  
substantially one index of refraction of the highly bire-  
fringent material. For example, a layer of isotropic  
30 material having an index of refraction matching substant-  
ially one index of refraction of the highly birefringent  
layer can be suitably bonded to the layer of highly bire-  
fringent polymer. A preferred device comprises a layer of  
the molecularly oriented and highly birefringent material  
35 bonded between two layers of isotropic material, the index

1 of refraction of each isotropic layer constituting sub-  
stantially a match with an index of refraction of the  
molecularly oriented and highly birefringent material.  
Such preferred device can be utilized for the polarization  
5 of light and may be termed a "total transmission" light  
polarizer, i.e., one which is particularly adapted to  
polarize a very large portion of incident light. Total  
polarizers find application in equipment such as may be  
employed for signaling, projection and display purposes,  
or the like, and in anti-glare systems for automotive  
10 vehicles.

According to another embodiment of the present invention,  
a molecularly oriented and highly birefringent material as  
defined herein can be suitably bonded to an additional  
15 layer of birefringent material. In such an embodiment, one  
index of refraction of the molecularly oriented and highly  
birefringent material will match substantially one index of  
refraction of the additional birefringent material. Similar-  
ly, the second index of refraction of the molecularly  
20 oriented and highly birefringent material will be sub-  
stantially a mismatch with respect to the second index of  
refraction of the additional birefringent material. Where  
a layer of molecularly oriented and highly birefringent  
material is bonded to an additional layer of birefringent  
25 birefringent material, the direction of orientation of each contiguous  
birefringent material will be substantially perpendicular  
with respect to the other.

According to another embodiment of the present invention,  
30 a plurality of alternating isotropic and birefringent  
layers can be utilized for the production of a multilayer  
light polarizing device, at least one of the layers of  
birefringent material comprising a molecularly oriented  
and highly birefringent material as defined herein. Such a  
35 device can be utilized as a multilayer polarizer which

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1 partly transmits and partly reflects incident light as  
separate linearly polarized components vibrating in ortho-  
gonal directions.

In Fig. 5 is shown, in considerably exaggerated dimensions,  
5 an optical device of the present invention in the form of  
light-polarizing sheet material 10 as it would appear in  
cross-section, namely, as viewed along a given edge. In  
order of arrangement with respect to the direction of a  
collimated beam 12 from a light source (not shown) the  
10 material is composed of an isotropic, or at least function-  
ally isotropic layer 14 having a relatively low refractive  
index, a molecularly oriented highly birefringent polymeric  
layer 16 and a functionally isotropic layer 18 having a  
relatively high refractive index, the layers preferably be-  
15 ing laminated or bonded together to form a unitary structure.  
It is not essential to the proper functioning of the device  
that the layers thereof be bonded together, provided, how-  
ever, that adjacent or contiguous layers enclosing an air  
layer are maintained parallel to one another. One refract-  
20 ive index of the polymeric molecularly oriented and highly  
birefringent layer 16 matches substantially that of  
layer 14 while the other refractive index thereof matches  
substantially the index of refraction of layer 18. For  
purposes of illustration, the aforesaid refractive indices  
25 may be taken as follows: the refractive index of layer 14  
is 1.50; the two indices of layer 16 are 2.00 and 1.50;  
and the index of layer 18 is 2.00.

The interface between layers 14 and 16 is composed of a  
30 plurality of lens-like or lenticular elements 16a and the  
interface between layers 16 and 18 is composed of a  
plurality of lens-like or lenticular elements 16b. It will  
be noted that the lenticules of one interface are offset,  
laterally, with respect to those of the other. The term  
35 "lenticular", as employed herein, may broadly be inter-

1 preted as constituting a plurality of surface configurations,  
including prismatic elements, as well as those of a strictly  
lens-like form. A certain degree of latitude is possible as  
to the choice of materials employed in forming the several  
layers. Thus, for example, layer 14 may suitably be composed  
5 of an isotropic plastic material such as poly(methylmeth-  
acrylate) having a refractive index of 1.50. Layer 16 can,  
accordingly, be composed of a transparent plastic layer which  
for example, has been rendered birefringent as by unidirect-  
ional stretching. Suitable for this purpose is the polymeric  
10 material, poly[2,2'-bis(trifluoromethyl)-4,4'-biphenylene]<sup>2</sup>,  
2'-dimethoxy-4,4'-biphenyldicarboxamide having refractive  
indices of 1.50 and 2.00 when thus rendered birefringent.  
Layer 18 can be suitably comprised of or incorporate a trans-  
parent isotropic material having an index of refraction  
15 approximating the higher index of birefringent layer 16.

One such material is poly(2,2'-dibromo-4,4'-biphenylene)-  
4,4'-stilbenedicarboxamide having an index of refraction  
of 2.07. Alternatively, layer 18 can comprise poly(2,2'-di-  
20 bromo-4,4'-biphenylene)- $\alpha$ -bromo-4,4'-stilbenedicarbox-  
amide having a refractive index of 2.05.

One method of constructing the sheet material is to form the  
birefringent layer 16 by a casting, or a casting and  
25 embossing procedure, after its proper solidification, and  
- casting the isotropic layers 14 and 18 on the opposite  
lenticular surfaces thereof. The birefringent layer 16 may  
be composed of substantially any material having a bire-  
fringence adapted to facilitate the required separation of  
30 light ray components and having indices of refraction which  
bear a proper relation to those of the contiguous layers 14  
and 18. It may also be formed by any of several different  
procedures. Assuming, by way of illustration, that the bi-  
refringence of layer 16 is to be achieved through its  
35 molecular orientation, a sheet or film of properly deform-

1 able material, such as the aforementioned material,  
poly[2,2'-bis(trifluoromethyl)-4,4'-biphenylene]-2",2"-  
dimethoxy-4",4"-biphenyldicarboxamide, i.e. a sheet of a  
given length and predetermined thickness, can be first  
extruded or cast. The sheet can then be subjected to a  
5 mechanical stress in a longitudinal direction to elongate  
and molecularly orient it, as by a stretching operation in  
the presence of heat or other softening agent, or by a cold  
drawing method, or, again, by applying a mechanical stress  
to its surface. The direction of stretch or other applicat-  
10 ion of orienting stress is to be taken as having been per-  
formed toward and away from the viewer, namely, in a  
direction normal to the plane of the paper. This being the  
case, the optic axis 20 of layer 16 constitutes a direction  
both in the plane of layer 16 and normal to the plane of the  
15 paper.

Birefringent layer 16, having acquired the desired bire-  
fringence as, for example, a birefringence of 1.50 and 2.00,  
assuming the stated refractive indices, can then be sub-  
20 jected to surface modification to form thereon the converg-  
ing or positive lenticular elements 16a and the diverging  
but functionally converging or positive lenticular ele-  
ments 16b. This can be suitably performed by passing the  
material between embossing means such as embossing blades,  
25 wheels or the like, the surfaces being slightly softened as  
by a solvent or heat, or both, as may be necessary during  
their treatment but not to such an extent as would relax  
the material and alter the previously provided orientation  
and birefringence. The embossing procedure is preferably  
30 performed in a direction along that of the optic axis, to  
facilitate preservation of the given orientation. Accord-  
ingly, the lenticules, as illustrated, are generally  
cylindrical with their axes extending parallel to the  
optic axis. As will be apparent and explained in further  
35 detail below, the lenticules play a major role in the

1 predetermined separation and focusing of the respective  
rays. While lenticular means of the type described con-  
stitute one preferred configuration, they may be so formed  
as to extend in other directions of the sheet or even have  
a spherical shape, provided that their refractive  
5 characteristics are properly chosen and the birefringence  
of the material is suitable. Alternatively, the lenticules  
may be formed by a grinding and polishing procedure or the  
sheet may be stretched or otherwise treated for orienting  
its molecules after the lenticules have been formed thereon.

10

After completion of the surfacing of the birefringent  
layer 16 and either prior to or after its orientation, the  
isotropic layers 14 and 18 are assembled therewith or formed  
thereon by any appropriate method such as by casting them  
15 in liquid form on the preformed layer 16. Assuming that the  
material of layers 14 and 18 is not of a type to cause any  
disturbing double refraction of light rays when solidified  
and subjected to mechanical stress, as by stretching, the  
stretching and desired molecular orientation of layer 16  
20 may be accomplished after casting and solidifying layers 14  
and 18 on its surfaces, the entire sheet 10 then being  
stretched as a unit. Or, the layers 14 and 18 may be cast  
on layer 16 after orientation of the latter. Alternatively,  
and again assuming layers 14 and 18 to be substantially  
25 incapable of becoming birefringent when stressed, they may  
be preformed so as to have the lenticular surfaces shown,  
superimposed in correctly spaced relation, the bire-  
fringent layer 16 formed therebetween in a fluid state and  
solidified, and the entire unit then stretched. In a further  
30 modification, the layers 14 and 18 may be preformed and  
assembled with layer 16, in either a bonded or non-bonded  
relation therewith, after the layer 16 has been treated to  
acquire a proper birefringence.

35 It has been noted with reference to Fig. 5, that the



1 lenticules 16a and 16 b are relatively offset from left to  
right, that is transversely of the sheet 10, so that the  
vertices of lenticules 16a are optically aligned with the  
longitudinal edges or intersections of lenticules 16b.  
While the lenticules 16a and 16b are shown as being  
5 spherical and of similar radii of curvature it will be  
understood that neither of these conditions is essential,  
per se, the choice depending in general upon the direction  
in which the rays are required to be refracted, the extent  
of their travel in said directions, and such factors as the  
10 refractive indices and thicknesses of the layers.

The collimated beams 12, emanating, for example, from a  
light source and reflector of a headlamp (not shown) and  
normally incident upon the isotropic layer 14, are trans-  
15 mitted without deviation through the latter to the converg-  
ing cylindrical lenticules 16a of birefringent layer 16.  
At layer 16 each beam is resolved into two components, that  
is an ordinary or "O" ray 12a and an extraordinary or "E"  
ray 12b. Bearing in mind that the refractive index of  
20 isotropic layer 14 has been given as 1.50 and the refractive  
indices of birefringent layer 16 as 1.50 and 2.00 let it be  
assumed that the 1.50 refractive index applies to the  
components 12a which, for purposes of illustration, will be  
considered the ordinary rays vibrating substantially at  
25 right angles to the optic axis. Inasmuch as these rays have  
a refractive index which is essentially identical to that  
of layer 14, which precedes layer 16 in order of their  
travel, they are refracted by lenticules 16b so to converge  
generally toward a theoretical focal plane, not shown. The  
30 rays 12a pass through isotropic layer 14 without deviation  
inasmuch as the refractive index of 1.50 and that of  
layer 14 are substantially identical. The components 12b,  
which in this instance are taken as the extraordinary rays  
vibrating in a plane passing through or parallel with the  
35 optic axis and having a refractive index of 2.00 identical

1 to that of the isotropic layer 18, are refracted by the  
lenticules 16a because of the dissimilarity of respective  
refractive indices. However, the diverging or negative  
lenticular surface 16a constitutes, in effect a converging  
lenticular surface of isotropic layer 14, the components 12b  
5 thereby being refracted convergently toward the aforesaid  
theoretical focal plane. As described, the layer 16 is  
positively birefringent inasmuch as the refractive index  
of the E ray is represented as greater than that of the  
O ray, but a reverse condition is possible. The rays 12a  
10 and 12b, generated in birefringent layer 16 are plane  
polarized, their vibration directions being at  $90^\circ$  to one  
another as indicated. The rays are thence transmitted without  
alteration of their state of polarization with their vibr-  
ational planes normal to one another.

15 Either the E or the O ray, or both, may be selectively  
treated, as by passing them through retardation materials,  
to provide their vibrations in a single azimuth as will be  
described below. Even without such treatment and a non-  
20 uniformity of vibration directions, the sheet material of  
Fig. 5 has certain uses such, for example, as for  
illumination purposes where it is desired to polarize the  
light partially in a given direction; for three-dimensional  
viewing or for any function wherein transmission of a large  
25 part of the incident light is of importance but wherein  
completely uniform polarization throughout a given area is  
not essential. While the entering rays 12 are shown as  
collimated at  $90^\circ$  to the plane of the sheet, a slight  
departure from this condition, from left-to-right in the  
30 drawing, can exist without preventing operation of the  
device of Fig. 5 or of others illustrated herein and a wide  
deviation therefrom may exist in a direction along the  
axis of the lenticules.

35 Consistent with obtaining an operational refraction or non-

refraction of rays generally similar to that shown in Fig. 5, the several layers may be formed of substantially any materials having suitable refractive indices, transparency and physical or mechanical properties such as thermal stability, flexibility or adhesion. Thus, for example, layer 14 may be composed of any of such materials as tetrafluoroethylene, vinyl acetate, cellulose acetate butyrate, an acrylic material, glass or the like. Birefringent layer 16 can be, for example, poly[2,2'-bis(trifluoromethyl)-4,4'-biphenylene]-4",4"'-stilbenedicarboxamide having indices of refraction 1.61 and 2.48 or a layer of poly(2,2'-dibromo-4,4'-biphenylene)-4",4"'-stilbenedicarboxamide having indices of 1.77 and 2.64. Layer 18 can be a polymeric material which has been rendered birefringent but which has its optic axis or direction of molecular orientation at 90° to that of layer 16, it being understood that its lenticular surface would match with that of layer 16 at 16b.

In an optical device of the present invention, the indices of refraction of the several layers can be modified or adjusted in predetermined manner such that the proper functional relation between the indices of refraction of the several layers is maintained. Thus, the indices of refraction of the several layers may be controlled in predetermined fashion by altering plasticizer content. For example, the index may be lowered by the addition of plasticizer. Where bonding substances or subcoats are employed in laminating preformed layers, a material used for such a purpose should have an index of refraction similar to that of one of the layers undergoing bonding to prevent unwanted reflection.

According to another embodiment of the present invention there is provided a light-polarizing element comprising a prismatic layer of molecularly oriented birefringent material and an isotropic or functionally isotropic layer.

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- 1 Such an element can be utilized in a device such as the headlamp of an automotive vehicle.

In Fig. 6 there is shown a headlamp 30 which includes a specularly reflecting parabolic mirror 32, a filament 34, a diffusely reflecting plate element 36 and a light-polarizing sheet material 40. Light-polarizing element 40 includes a prismatic layer 42 of molecularly oriented and highly birefringent polymer and an isotropic layer 44, the refractive index of the isotropic layer 44 substantially matching the low index of refraction of birefringent layer 42. Thus, for example, birefringent layer 42 may have refractive indices of 2.00 and 1.50 and layer 44 a refractive index of 1.50. An unpolarized collimated beam 12, upon entering birefringent layer 42, is resolved into O and E components 12a and 12b, as previously described in connection with the device shown in Fig. 5. The prism elements of birefringent layer 42 are so formed and disposed relative to the incident collimated beam 12 that the E ray 12b is reflected rearwardly to the parabolic mirror 32, is reflected to diffusely reflecting element 36, whereat it is depolarized, is reflected to mirror 32 and thence to light-polarizing sheet material 40 as a second collimated unpolarized beam 12d. The prism elements, may for this purpose, appropriately be prisms or so-called hollow corner cubes which have the characteristic of reflecting collimated light rays in the direction whence they came. The O ray 12a is transmitted without deviation straight through layer 44 which matches its refractive index. This procedure repeats itself, ad infinitum, it being apparent that eventually substantially all of the light from source 34 is transmitted in the form of collimated O rays having a uniform azimuth of polarization.

According to still another embodiment of the present invention, there is provided a multilayer light-polarizing

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1 device effective to linearly polarize a large portion of  
the light incident thereon and to transmit substantially  
all of one polarized component of light while reflecting  
substantially all of the orthogonally polarized component.  
Such a polarizer is shown in Fig. 7 as polarizer 50 having  
5 alternate layers 54 and 56 of molecularly-oriented, highly-  
birefringent material and of isotropic or functionally iso-  
tropic material.

The layers 54 are each composed of a molecularly oriented  
10 birefringent material. For instance, the material may  
comprise poly[2,2'-bis(trifluoromethyl)-4,4'-biphenylene] 2",  
2"-dimethoxy-4",4"-biphenyldicarboxamide. Other materials  
can also be utilized in forming the birefringent layer and  
should be selected to have as great a difference between the  
15 two indices of refraction as possible since the number of  
layers in the polarizer can be substantially decreased when  
using birefringent materials having a greater difference  
between their indices of refraction.

20 The isotropic layers 56 may be composed of a number of  
different materials with the requirement that its refract-  
ive index substantially match one of the refractive indices  
of the birefringent material layers on either side thereof.  
Some examples of materials which are useful for this  
25 purpose include polyacrylates, poly(2,2'-dibromo-4,4'-bi-  
phenylene)4",4"-stilbenedicarboxamide, silicon oxides or  
titanium dioxides. The isotropic layers can be provided,  
for example, by vacuum deposition so that their thickness  
can be precisely controlled. Alternately, the isotropic  
30 layer may be co-extruded simultaneously with the birefringent  
layers interleaved therebetween.

As shown in Fig. 7 the optical axis 58 of each birefringent  
layer lies in a plane parallel to the planar substrate  
35 surface 60. This is accomplished, for example, through the

1 use of a stretch orientation operation. Layer thickness  
can be suitably controlled by the extrusion process and  
allowances for dimensional changes expected in the layer  
thickness during the stretching step can be made.

5 Fig. 7 schematically shows a number of light rays 62 in-  
cident on polarizer 50 and traveling in a direction per-  
pendicular to the surface thereof. As an example, the bi-  
refrinent layers 54 may have a pair of refractive indices  
of  $n_o = 1.50$  and  $n_E = 2.00$  and the refractive index of each  
10 isotropic layer may be taken as  $n = 1.50$ . As each ray 62  
passes through the first birefringent layer 54, it is  
resolved thereby into two components shown as separate  
rays, namely, an extraordinary or "E" ray 62a for which the  
birefringent layer has the higher index  $n_E = 2.00$  and an  
15 ordinary ray or "O" ray 62b for which the birefringent layer  
has, for example, the lower index  $n_o = 1.50$ , the rays  
traveling in a similar direction and with their vibration  
azimuths relatively orthogonally disposed as depicted in  
the drawing. As shown in Fig. 7, a portion 62c of the "E"  
20 rays 62a is reflected at the first interface 64 reached, it  
being recalled that the refractive index of an isotropic  
layer was given at  $n = 1.50$ . The reflection is due to the  
refractive index discontinuity at the interface between the  
layers 54 and 56 which exists for the "E" polarization but  
25 not the "O" polarization. For purposes of illustration the  
reflected light rays 62c are shown as being reflected at a  
slight angle while in actuality they are reflected straight  
back in the direction of rays 62a. Thereafter each interface  
such as 66 and 68 will reflect a further portion of ray 62a.  
30 The rays 62b are unreflected at the interface 64 because  
the refractive index for "O" rays 62b in layer 54 matches  
that of layer 56 and in fact, these rays 62b will pass  
through all layers 54 and 56 unreflected and comprise that  
portion of the light incident on the polarizer that is  
35 transmitted thereby.

1 In order to greatly increase the reflectivity of the  
polarizer 50 each layer 54 and 56 is made to have an  
optical thickness of one-quarter the length of a selected  
wavelength. The optical thickness is equal to the physical  
thickness multiplied by the index of refraction of the  
5 layer material. The wavelength selected is preferably in  
the middle of the visible spectrum, for example, 550 nm so  
that the polarizer is effective over a substantial range of  
visible light. This arrangement utilizes optical inter-  
ference to enhance the efficiency of the polarizer. The  
10 following discussion relates to phase changes in a light  
wave, not to changes in the polarization azimuth of the  
light wave. In analyzing the optical properties of the  
polarizer, it is important to remember that light suffers a  
phase change of  $\pi$  on reflection when it goes from a medium  
15 of low refractive index to a medium of higher refractive  
index while it suffers no phase change on reflection when  
it goes from a medium of high refractive index to a medium  
with a lower refractive index. Thus, in Fig. 7, a light  
ray such as 62a, as it passes through the first quarter-  
20 wave birefringent layer 54 will suffer a phase change  $\pi/2$ .  
As the light ray strikes the first interface 64 part of it  
is reflected back through the first birefringent layer 54  
again suffering a phase change of  $\pi/2$ , the total phase  
change being equal of  $\pi/2 + \pi/2 = \pi$ . Note that the ray 62a  
25 suffers no phase change on reflection at interface 64 due  
to the rule as stated above. Now as the remaining portion of  
ray 62a strikes the second interface 66, it has traveled  
through two layers suffering a phase change of  $\pi/2 + \pi/2$   
in one direction and  $\pi/2 + \pi/2$  on reflection. The ray 62a  
30 will also suffer a phase change of  $\pi$  on reflection due to  
the above rule and the total phase change will equal  
 $4\pi/2 + \pi$  or  $3\pi$ . Thus, in accordance with this analysis,  
the ray 62a will always suffer a phase change of some  
multiple of  $\pi$  as it is reflected from each and every inter-  
35 face in the multilayer polarizer. Each reflected

1 component 62c of ray 62a and other such similar rays will  
reinforce one another resulting in substantially total  
reflection of the one polarized component of incident  
light represented by ray 62a providing the number of layers  
and interfaces are sufficient. The other component 62b  
5 will pass undisturbed through the multilayer polarizer 50  
so long as the refractive index of the isotropic layers 56  
match one of the refractive indices of the birefringent  
layers 54. Since substantially none of the rays 62a are  
transmitted, the entire amount of light output from  
10 polarizer 50 consists of rays 62b, all polarized in one  
direction.

In Fig. 8 is shown an optical beam-splitter device of the  
present invention embodying a layer of birefringent poly-  
15 mer. Beam splitter 70 comprises prisms 72a and 72b of iso-  
tropic material such as glass joined in a Nicol configurat-  
ion with a layer 74 of molecularly oriented birefringent  
polymer therebetween. Elements 72a and 72b can be composed  
of a variety of glass or other isotropic materials and  
20 will have a perpendicular index of refraction greater than  
that of the polymer layer 74 between such elements. For  
example, a unidirectionally stretched layer 74 of poly-  
[2,2'-bis(trifluoromethyl)-4,4'-biphenylene]-2,2'-dimethoxy-  
4,4'-biphenyl having a perpendicular index of refraction of  
25 about 1.65 and a unidirectional stretch direction as  
indicated in Fig. 8 can be utilized between isotropic glass  
elements 72a and 72b of refractive index 1.8. In operation,  
unpolarized light 76 enters element 72a and a portion  
thereof is reflected at the interface of element 72a and  
30 layer 74 so as to emerge as plane-polarized light 78. A  
portion of light 76 is refracted by layer 74 and emerges  
from element 72b as oppositely plane-polarized light 80.  
Light 76 is thus split into separate beams of oppositely  
polarized light by beam splitter 70.



1 While particular embodiments of the present invention  
utilizing polymeric birefringent layers have been described  
in connection with the devices shown in Figs. 5 to 7,  
other devices utilizing such polymeric birefringent layers  
can also be prepared. Examples of other devices which can  
5 be adapted to include a polymeric and highly birefringent  
layer as described herein are described, for example, in  
U.S. Patent 3,506,333 (issued April 14, 1970 to E.H. Land);  
in U.S. Patent 3,213,753 (issued October 26, 1965 to H.G.  
Rogers); in U.S. Patent 3,610,729 (issued October 5, 1971  
10 to H.G. Rogers); in U.S. Patent 3,473,013 (issued  
October 14, 1969 to H.G. Rogers); in U.S. Patent 3,522,984  
(issued August 4, 1970 to H.G. Rogers); in U.S. Patent  
3,522,985 (issued August 4, 1970 to H.G. Rogers); in U.S.  
Patent 3,528,723 (issued September 15, 1970 to H.G. Rogers);  
15 and in U.S. Patent 3,582,424 (issued June 1, 1971 to K.  
Norvaisa). Still other devices that can be prepared  
utilizing a birefringent polymer hereof include Wollaston  
prisms, Rochan prisms, Fuessner prisms, Brewster polarizers,  
non-polarizing beam splitters, compensators and the like.

20 The following non-limiting examples are illustrative of  
the present invention.

#### Example 1

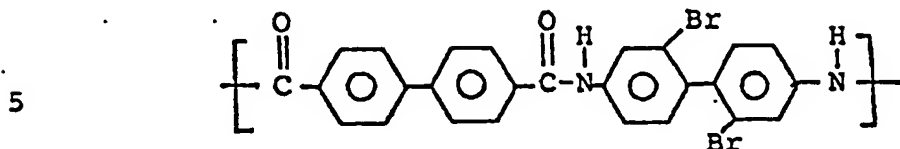
25 This example illustrates the preparation of poly(2,2'-di-  
bromo-4,4'-biphenylene)-p,p'-biphenylene dicarboxamide and  
the preparation therefrom of birefringent polymeric films.

30 A 50-ml reaction vessel (a resin-making kettle equipped with  
a mechanical stirrer, nitrogen inlet tube and calcium  
chloride drying tube) was heated while simultaneously  
flushing the vessel with nitrogen. After the reaction  
vessel had cooled to room temperature, 1.63 g of anhydrous  
35 lithium chloride and 0.5746 g (0.001679 mole) of sublimed

1 2,2'-dibromobenzidine were added while maintaining a  
positive nitrogen pressure. The reaction vessel was fitted  
with a thermometer and a rubber stopple (a rubber membrane-  
like sealing lid capable of receiving a syringe and of  
5 sealing itself upon removal of the syringe). 10 ml of an-  
hydrous distilled N-methylpyrrolidone (NMP) and 15 ml of  
anhydrous distilled tetramethylurea (TMU) were carefully  
added with the aid of syringes. The resulting mixture was  
stirred and warmed to 40°C until all solids had dissolved.  
The solution was then cooled in a bath of ice and salt to a  
10 temperature of -5°C. A small amount of lithium chloride  
precipitation was observed. Recrystallized p,p'-biphenylene  
dicarbonyl chloride (0.4689 g; 0.001679 mole) was quickly  
added by means of a funnel to the stirred 2,2'-dibromo-  
benzidine solution. An additional 5 ml of TMU were added  
15 through the funnel to the reaction mixture. The temperature  
of the reaction mixture did not rise above a temperature of  
7°C. After stirring for 60 minutes, the reaction mixture  
began to thicken and streaming birefringence (but not stir  
opalescence) was observed.

20 The ice bath was removed from the reaction vessel and the  
temperature was observed to rise to 20°C in 30 minutes at  
which point the reaction solution became milky in appear-  
ance. The reaction vessel was placed in an oil bath (40°C)  
25 and the reaction mixture was warmed for 30 minutes. The  
reaction mixture became clear. The temperature of the  
reaction mixture rose during the warming to a maximum  
temperature of 55°C at which temperature the reaction  
mixture was stirred for 1 hour. The reaction product, a  
30 3 % wt./vol. polymer solution (3 g of polymer per 100 ml  
of reaction solvent) was cooled to 40°C and poured into  
200 ml of ice-water in a blender. The resulting fibrous  
solid was filtered and washed (in the blender) twice each  
with water, acetone and ether. The product was dried in a  
35 vacuum oven at 15 mm pressure and 90°C for 18 hours. The

- 1 product, obtained in 95.4 % yield, was a white fibrous  
polymeric material having the following recurring  
structural units:



- 10 The inherent viscosity of a polymer solution (0.5 g of the  
polymer of Example 1 per 100 ml of a solution of 5 g  
lithium chloride per 100 ml of dimethylacetamide) was  
3.54 dl/g at 30°C.

- 15 Molecular structure was confirmed by infrared spectroscopy.  
Inspection of the ultraviolet/visible absorption spectrum  
for the polymer of Example 1 (in 5 % wt./vol. lithium  
chloride/dimethylacetamide) showed a  $\lambda_{\max}$  of 320 ( $\epsilon = 75,000$ ).

Elemental analysis for  $C_{26}H_{16}Br_2N_2O_2$  provided the following:

20

	%C	%H	%Br	%N	%O
Calculated:	56.97	2.92	29.16	5.11	5.84
Found:	56.86	3.25	28.72	5.10	6.07 (by differ- ence)

- 25 Polymeric films were prepared from the polymeric material of  
Example 1 by casting (onto glass plates) solutions of the  
polymeric material in a 5 % wt./vol. solution of lithium  
chloride and dimethylacetamide (5 g lithium chloride per  
100 ml of dimethylacetamide). The concentration of polymer  
30 ranged from 0.5 to 5 % wt./vol., i.e., from 0.5 g to 5 g  
polymer per 100 ml of the lithium chloride/dimethylacetamide  
solution. In each instance, the glass plate carrying the  
puddle-cast polymer solution was immersed in water (after  
minimal evaporation of solvent). The polymer film was ob-  
35 served to gel and a transparent and colourless unoriented

1 film separated from the glass plate. The resulting film  
was soaked for several hours in water to effect extraction  
of occluded lithium chloride and solvent, soaked in acetone  
and dried in a vacuum oven at 90°C and 15 mm pressure.  
Refractive index, measured by interferometry, was 1.93,

5 Stretched polymeric films were prepared in the following  
manner. Water-swollen films (obtained by soaking the poly-  
mer films for several hours for removal of occluded lithium  
chloride and solvent as aforescribed) were cut into  
10 strips. The strips were mounted between the jaws of a  
mechanical unidirectional stretcher. The strips were  
stretched (in air at 220°C) to about 50 % elongation, to  
effect film orientation. The resulting films were optically  
transparent. Birefringence, measured with the aid of a  
15 quartz wedge, was 0.293.

#### Example 2

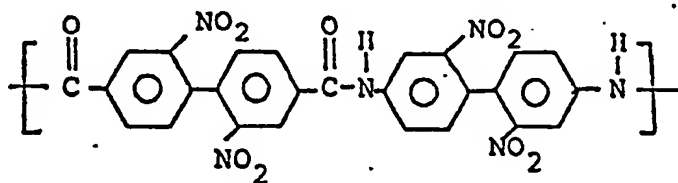
20 This example illustrates the preparation of poly(2,2'-di-  
nitro-4,4'-biphenylene)-o,o'-dinitro-p,p'-biphenylene di-  
carboxamide and the preparation therefrom of birefringent  
polymeric films.

25 A 50 ml reaction vessel (a resin-making kettle equipped  
with a mechanical stirrer, nitrogen inlet tube and calcium  
chloride drying tube) was heated while simultaneously  
flushing the vessel with nitrogen. After the reaction  
vessel had cooled to room temperature, 1.5 g of anhydrous  
lithium chloride and 0.4799 g (0.001750 mole) of re-  
30 crystallized 2,2'-dinitrobenzidine yellow crystals were  
added while maintaining a positive nitrogen pressure. The  
reaction vessel was fitted with a thermometer and a rubber  
stopples and 30 ml of anhydrous distilled N-methylpyrrol-  
idone (NMP) and 20 ml of anhydrous distilled tetramethyl-  
35 urea (TMU) were carefully added with the aid of syringes.

1 The resulting mixture was stirred and warmed to 40°C until  
all solids had dissolved. The solution was then cooled in a  
bath of ice and salt to a temperature of -5°C. Recrystalliz-  
ed colourless 2,2'-dinitro-4,4'-biphenyl dicarbonyl  
chloride (0.6460 g; 0.00175 mole) was quickly added by  
5 means of a funnel to the stirred 2,2'-dinitrobenzidine  
solution. An additional 3 ml of NMP were added through the  
funnel to the reaction mixture. The temperature of the  
reaction mixture did not rise above a temperature of 0°C.  
After stirring for 30 minutes, there was no noticeable  
10 change in reaction mixture viscosity.

The ice bath was removed from the reaction vessel and the  
temperature was observed to rise to 20°C in 30 minutes at  
which point the reaction solution was heated in stages up  
15 to 90°C over a period of 2.5 hours.

The reaction product, a 3 % wt./vol. polymer solution  
(3 g of polymer per 100 ml of reaction solvent) was cooled  
to 40°C and poured into 200 ml of ice-water in a blender.  
20 The resulting gelatinous solid was filtered and washed (in  
the blender) twice each with water, acetone and ether. The  
product was dried in a vacuum oven at 15 mm Hg pressure and  
90°C for 18 hours. The polymeric product, obtained in 88 %  
yield, was a dark-yellow powder having the following re-  
25 ccurring structural units:



30

The inherent viscosity of a polymer solution (0.5 g of the  
polymer of Example 2 per 100 ml of a solution of 5 g  
lithium chloride per 100 ml of dimethylacetamide) was  
35 1.40 dl/g at 30 °C.

- 1 Molecular structure was confirmed by infrared spectroscopy. Inspection of the ultraviolet/visible absorption spectrum for the polymer of Example 2 (in 5 % wt./vol. lithium chloride/dimethylacetamide) showed a  $\lambda_{\text{max}}$  of 307 nm ( $\epsilon = 38,400$ ) and an absorption peak at 365 nm ( $\epsilon = 3,000$ ).

Elemental analysis for  $\text{C}_{26}\text{H}_{14}\text{N}_6\text{O}_{10}$  provided the following:

	<u>%C</u>	<u>%H</u>	<u>%N</u>	<u>%O</u>
10 <u>Calculated:</u>	54.74	2.47	14.73	28.06
<u>Found</u>	54.24	2.60	13.91	29.25 (by difference)

- 15 Thermogravimetric analysis showed that onset of degradation of the polymer of Example 2 occurred at 360°C in nitrogen and at 300°C in air. Differential scanning calorimetry and thermal mechanical analysis of film samples showed a reproducible transition at about 190°C.

- 20 Polymeric films were prepared from the polymeric material of Example 2 by casting (onto glass plates) a solution of the polymeric material in a 5 % wt./vol. solution of lithium chloride and dimethylacetamide (5 g lithium chloride per 100 ml of dimethylacetamide). The concentration of polymer was 5 % wt./vol., i.e., 5 g polymer per 100 ml of the lithium chloride/dimethylacetamide solution. In each instance, the glass plate carrying the puddle-cast polymer solution was immersed in water (after most of the solvent had evaporated). The polymer film was observed to gel and a transparent, yellow unoriented film separated from the glass plate. The resulting film was soaked for several hours in water to effect extraction of occluded lithium chloride and solvent.

- 35 Stretched polymeric films were prepared in the following manner. Water-swollen films (obtained by soaking the poly-

mer films for several hours for removal of occluded lithium chloride and solvent as aforescribed) were cut into strips. The strips were mounted between the jaws of a mechanical unidirectional stretcher. The strips were stretched (in boiling ethylene glycol) to about 60 % elongation, to effect film orientation. The resulting polymeric strips were optically transparent. Birefringence, measured with the aid of a quartz wedge, and by index matching, was 0.33. The calculated isotropic refractive index was 1.75. Wide-angle X-ray analysis of the birefringent films showed crystallinity to be less than 10 % by weight.

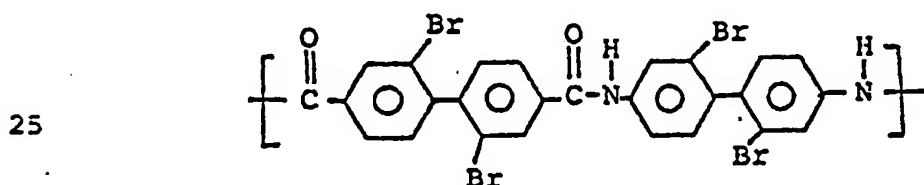
### Example 3

This example illustrates the preparation of poly(2,2'-dibromo-4,4'-biphenylene)-o,o'-dibromo-p,p'-biphenylene dicarboxamide and the preparation therefrom of birefringent polymeric films.

A 50 ml reaction vessel (a resin-making kettle equipped with a mechanical stirrer, nitrogen inlet tube and calcium chloride drying tube) was heated while simultaneously flushing the vessel with nitrogen. After the reaction vessel had cooled to room temperature, 2.0 g of anhydrous lithium chloride and 0.7828 g (0.002289 mole) of sublimed 2,2'-dibromobenzidine were added while maintaining a positive nitrogen pressure. The reaction vessel was fitted with a thermometer and a rubber stopple and 20 ml of anhydrous distilled N-methylpyrrolidone (NMP) and 35 ml of anhydrous distilled tetramethylurea (TMU) were carefully added with the aid of syringes. The resulting mixture was stirred and warmed to 40°C until all solids had dissolved. The solution was then cooled in a bath of ice and salt to a temperature of 0°C. Recrystallized 2,2'-dibromo-4,4'-biphenylene dicarbonyl chloride (1.0000 g; 0.002289 mole) was quickly

1 added by means of a funnel to the stirred 2,2'-dibromobenz-  
idine solution. An additional 5 ml of TMU, at a temperature  
of 25°C, were added through the funnel to the reaction  
mixture. The temperature of the reaction mixture rose to  
15°C and then dropped to 4°C. After stirring for 15 minutes,  
5 the reaction mixture began to thicken and streaming bire-  
fringence (but not stir opalescence) was observed. Stirring  
was continued for an additional 30 minutes at 7°C and the  
ice bath was removed from the reaction vessel. The temper-  
ature of the reaction mixture rose to 25°C (in 90 minutes)  
10 and the reaction mixture was then slowly heated to 100°C  
over a two-hour period.

The reaction product, a 4 % wt./vol. polymer solution  
(4 g of polymer per 100 ml of reaction solvent) was cooled  
15 to 40°C and poured into 200 ml of ice-water in a blender.  
The resulting fibrous solid was filtered and washed (in  
the blender) twice each with water, acetone and ether. The  
product was dried in a vacuum oven at 15 mm pressure and  
90°C for 18 hours. The product, obtained in 96.6 % yield,  
20 was a white fibrous polymeric material having the following  
recurring structural units:



The inherent viscosity of a polymer solution (0.5 g of the  
polymer of Example 3 per 100 ml of a solution of 5 g  
30 lithium chloride per 100 ml of dimethylacetamide) was  
2.04 dl/g at 30 °C. Molecular weight determination based  
on light scattering, indicated  $2.72 \times 10^5$ , and by gel  
permeation chromatography, a molecular weight of  $5.66 \times 10^4$ .  
35 Molecular structure was confirmed by infrared spectroscopy.



1 Inspection of the ultraviolet/visible absorption spectrum for the polymer of Example 3 (in 5 % wt./vol. lithium chloride/dimethylacetamide) showed a  $\lambda_{\text{max}}$  of 305 nm ( $\epsilon = 31,900$ ) and no absorption above 380 nm.

5 Elemental analysis for  $\text{C}_{26}\text{H}_{14}\text{Br}_4\text{N}_2\text{O}_2$  provided the following

	<u>%C</u>	<u>%H</u>	<u>%Br</u>	<u>%N</u>	<u>%O</u>
<u>Calculated:</u>	44.23	1.99	45.27	3.99	4.52
<u>Found:</u>	44.54	2.19	45.25	3.87	4.15

10

Thermogravimetric analysis showed that onset of degradation of the polymer of Example 3 occurred at 530°C in nitrogen. Thermal mechanical analysis of film samples showed a reproducible transition at about 120°C.

15

Polymeric films were prepared from the polymeric material of Example 3 by casting (onto glass plates) solutions of the polymeric material in a 5 % wt./vol. solution of lithium chloride and dimethylacetamide (5 g lithium chloride per 100 ml of dimethylacetamide). The concentration of polymer ranged from 0.5 to 5 % wt./vol., i.e. from 0.5 g to 5 g polymer per 100 ml of the lithium chloride/dimethylacetamide solution. In each instance, the glass plate carrying the puddle-cast polymer solution was immersed in water (after most of the solvent had evaporated). The polymer film was observed to gel and a transparent, colourless unoriented film separated from the glass plate. The resulting film was soaked for several hours in water to effect extraction of occluded lithium chloride and solvent, soaked in acetone and dried in a vacuum oven at 90°C and 15 mm Hg pressure. Refractive index, measured by interferometry, was 1.84.

35 Stretched polymeric films were prepared in the following manner. Water-swollen films (obtained by soaking the

1 polymer films for several hours for removal of occluded  
lithium chloride and solvent as aforescribed) were cut  
into strips. The strips were mounted for stretching between  
the jaws of a mechanical unidirectional stretcher. Strips  
were stretched, in some instances, in air at 220°C and, in  
5 other instances, in boiling ethylene glycol. Elongation  
ranged from 60 % to 65 %. Infrared dichroism indicated that  
the films were less than 65 % oriented. The films were  
optically transparent. Birefringence, measured with the aid  
of a quartz wedge, was 0.390. Wide-angle X-ray analysis of  
10 the birefringent polymer films showed them to be less than  
10 % by weight crystalline.

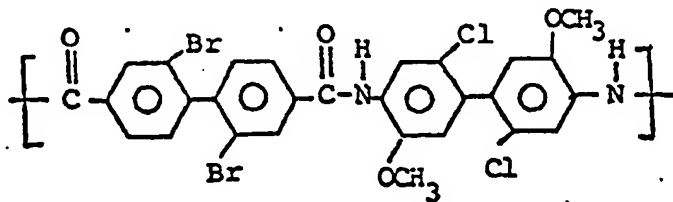
#### Example 4

15 This example illustrates the preparation of poly(2,2'-di-  
chloro-5,5'-dimethoxy-biphenylene)-o,o'-dibromo-p,p'-bi-  
phenylene dicarboxamide and the preparation therefrom of  
birefringent polymeric films.

20 A 50-ml reaction vessel (a resin-making kettle equipped with  
a mechanical stirrer, nitrogen inlet tube and calcium  
chloride drying tube) was heated while simultaneously  
flushing the vessel with nitrogen. After the reaction vessel  
had cooled to room temperature, 1.5 g of anhydrous lithium  
25 chloride and 0.6519 g (0.002082 mole) of sublimed 2,2'-di-  
chloro-5,5'-dimethoxybenzidine were added while maintaining  
a positive nitrogen pressure. The reaction vessel was fitted  
with a thermometer and a rubber stopple and 10 ml of an-  
hydrous distilled N-methylpyrrolidone (NMP) and 10 ml of  
30 anhydrous distilled tetramethylurea (TMU) were carefully  
added with the aid of syringes. The resulting mixture was  
stirred and warmed to 40°C until all solids had dissolved.  
The resulting orange solution was then cooled in a bath of  
ice and salt to a temperature of 0°C. A small amount of  
35 lithium chloride precipitation was observed. Recrystallized

1 2,2'-dibromo-4,4'-biphenyldicarbonyl chloride (0.9095 g;  
 0.002082 mole) was quickly added by means of a funnel to  
 the stirred 2,2'-dichloro-5,5'-dimethoxybenzidine solution.  
 An additional 10 ml of TMU (at a temperature of 25°C) were  
 added through the funnel to the reaction mixture. The  
 5 temperature of the reaction mixture did not rise above a  
 temperature of 0°C. After stirring for 30 minutes, the  
 formation of a gelatinous, light-yellow, transparent mass  
 (which exhibited streaming birefringence but not stir  
 opalescence) was observed. Stirring was continued for an  
 10 additional 10 minutes at 8°C, the stirring was stopped and  
 the ice bath was removed. The temperature of the reaction  
 mass was observed to rise to 25°C in 15 minutes, and the gel  
 became stiffer in consistency. Heating was immediately  
 commenced and an additional 20 ml of TMU were added to  
 15 facilitate dissolution of the reaction mass. Within  
 60 minutes the temperature rose to 90°C and the gel  
 melted to provide a homogeneous, viscous solution. Heating  
 at 90°C was continued for two hours while stirring vigor-  
 ously.

20 The reaction product, a 2.82 % wt./vol. light-yellow poly-  
 mer solution (2.82 g of polymer per 100 ml of reaction  
 solvent) was cooled to 40°C and the resulting gelatinous,  
 transparent mass was added to 200 ml of ice-water in a  
 25 blender. The resulting rubbery solid was filtered and  
 washed (in the blender) twice each with water, acetone and  
 ether. The product was dried in a vacuum oven at 15 mm Hg  
 pressure and 90°C for 18 hours. The product, obtained in  
 99.3 % yield, was a very pale-yellow fibrous polymeric  
 30 material having the following recurring structural units:



The inherent viscosity of a polymer solution (0.5 g of the polymer of Example 4 per 100 ml of a solution of 5 g lithium chloride per 100 ml of dimethylacetamide) was 5.75 dl/g at 30°C.

Molecular structure was confirmed by infrared spectroscopy. Elemental analysis for  $C_{28}H_{18}Br_2Cl_2N_2O_4$  provided the following:

	<u>%C</u>	<u>%H</u>	<u>%Br</u>	<u>%Cl</u>	<u>%N</u>	<u>%O</u>
<u>Calculated:</u>	49.66	2.68	23.60	10.47	4.14	9.45
<u>Found:</u>	49.05	2.95	23.07	--	4.15	--

Polymeric films were prepared from the polymeric material of Example 4 by casting (onto glass plates) solutions of the polymeric material in a 5 % wt./vol. solution of lithium chloride and dimethylacetamide (5 g lithium chloride per 100 ml of dimethylacetamide). The concentration of polymer was 2 % wt./vol., i.e., 2 g of polymer per 100 ml of the lithium chloride/dimethylacetamide solution. In each instance, the glass plate carrying the puddle-cast polymer solution was immersed in water (after minimal evaporation of solvent). The polymer film was observed to gel and a transparent, colourless unoriented film separated from the glass plate. The resulting film was soaked for 2 days in water to effect extraction of occluded lithium chloride and solvent, soaked in acetone and dried in a vacuum oven at 90°C and 15 mm pressure. Refractive index, measured by interferometry was 1.87.

Stretched polymeric films were prepared in the following manner. Water-soluble films (obtained by soaking the polymer films for several hours for removal of occluded lithium chloride and solvent as aforescribed) were cut into strips. The strips were

1 mounted between the jaws of a mechanical unidirectional  
stretcher. The strips were stretched (in air at 220°C) to  
about 50 % elongation, to effect film orientation. The  
stretched films were optically transparent. Birefringence,  
measured with the aid of a quartz wedge, was 0.24.

5 Solutions of the polymer of Example 4, in a concentration  
of 3 to 5 % wt./vol., in lithium chloride-containing  
solvents (e.g., dimethylacetamide containing lithium  
chloride) were found to form colourless, transparent gels  
10 which could be melted and resolidified without thermal  
degradation. When the molten solutions were poured into  
molds or cast into films, solidification was rapid and the  
solid pieces or films were readily removable. The resulting  
rubbery solids exhibited high birefringence upon application  
15 of very slight stress. Removal of the stress was accompanied  
by instantaneous disappearance of the birefringent property

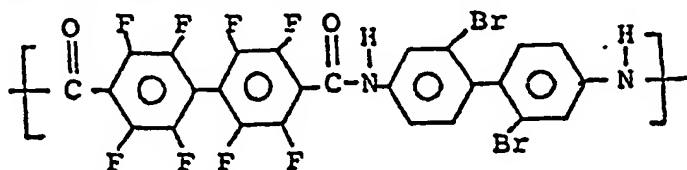
#### Example 5

20 This example illustrates the preparation of poly(2,2'-di-  
bromo-4,4'-biphenylene)-octafluoro-p,p'-biphenylene di-  
carboxamide and the preparation therefrom of birefringent  
polymeric films.

25 A 50-ml reaction vessel (a resin-making kettle equipped  
with a mechanical stirrer, nitrogen inlet tube and calcium  
chloride drying tube) was heated while simultaneously  
flushing the vessel with nitrogen. After the reaction  
vessel had cooled to room temperature, 1.5 g of anhydrous  
30 lithium chloride and 0.4571 g (0.001338 mole) of sublimed  
2,2'-dibromobenzidine were added while maintaining a  
positive nitrogen pressure. The reaction vessel was fitted  
with a thermometer and a rubber stopple and 10 ml of an-  
hydrous distilled N-methylpyrrolidone (NMP) and 10 ml of  
35 anhydrous distilled tetramethylurea (TMU) were carefully

- added with the aid of syringes. The resulting mixture was stirred and warmed to 40°C until all solids had dissolved. The solution was then cooled in a bath of ice and salt to a temperature of 0°C. A small amount of lithium chloride precipitation was observed. Distilled 2,2',3,3',5,5',6,6'-octafluoro-4,4'-biphenylene dicarbonyl chloride (0.5660 g; 0.001338 mole) was quickly added by means of a funnel to the stirred, 2,2'-dibromobenzidine solution. An additional 10 ml of TMU (at a temperature of 25°C) were added through the funnel to the reaction mixture. The temperature of the reaction mixture did not rise above a temperature of 2°C. After stirring for 15 minutes, the reaction mixture began to thicken and streaming birefringence (but not stir opalescence) was observed. Stirring was continued for an additional 30 minutes at 4°C and the ice bath was removed.
- 5 The temperature of the reaction mixture was observed to rise to 25°C in 40 minutes at which point the reaction solution was slightly viscous and cloudy in appearance. The reaction mixture was warmed gently for 90 minutes with stirring. The temperature of the reaction mixture rose
- 10 during the warming to a maximum temperature of 45°C at which temperature the reaction solution became homogeneous. Stirring was continued for 18 hours at 45°C.

- The resulting reaction product, a 3 % wt./vol. polymer solution (3 g of polymer per 100 ml of reaction solvent)
- 5 was cooled to 40°C and poured into 200 ml of ice-water in a blender. The resulting fibrous solid was filtered and washed (in the blender) twice each with water, acetone and ether. The product was dried in a vacuum oven at 15 mm
- 10 pressure and 90°C for 18 hours. The product, obtained in 87.6 % yield, was a white fibrous polymeric material having the following recurring structural units:



- 1 The inherent viscosity of a polymer solution (0.5 g of the polymer of Example 5 per 100 ml of a solution of 5 g lithium chloride per 100 ml of dimethylacetamide) was 1.68 dl/g at 30°C.
- 5 Molecular structure was confirmed by infrared spectroscopy. Inspection of the ultraviolet/visible absorption spectrum for the polymer of Example 5 (in 5 % wt./vol. lithium chloride/dimethylacetamide) showed a  $\lambda_{\text{max}}$  of 340 nm and an absorption peak at 360 nm ( $\epsilon = 306$ ).

10

Elemental analysis for  $\text{C}_{26}\text{H}_8\text{Br}_2\text{F}_8\text{N}_2\text{O}_2$  provided the following:

	<u>%C</u>	<u>%H</u>	<u>%Br</u>	<u>%F</u>	<u>%N</u>	<u>%O</u>
15 <u>Calculated:</u>	45.11	1.17	23.09	21.97	4.05	4.61
<u>Found:</u>	42.89	1.17	21.86	20.81	3.76	9.51
						(by difference)

- Thermogravimetric analysis showed that onset of degradation of the polymer of Example 5 occurred at 325°C in nitrogen and at 350°C in air. Differential scanning calorimetry showed a reproducible transition at about 155°C.
- 20

- Polymeric films were prepared from the polymeric material of Example 5 by casting (onto glass plates) solutions of the polymeric material in a 2 % wt./vol. solution of lithium chloride and dimethylacetamide (2 g lithium chloride per 100 ml of dimethylacetamide). The concentration of polymer ranged from 0.5 to 5 % wt./vol., i.e., from 0.5 g to 5 g polymer per 100 ml of the lithium chloride/dimethylacetamide solution. In each instance, the glass plate carrying the puddle-cast polymer solution was immersed in water (after minimal evaporation of solvent). The polymer was observed to gel and a transparent and colourless unoriented film separated from the glass plate.
- 30
- The resulting film was soaked for several hours in water to
- 35

effect extraction of occluded lithium chloride and solvent, soaked in acetone and dried in a vacuum oven at 90°C and 15 mm Hg pressure. Refractive index, measured by interferometry was 1.74.

Stretched polymeric films were prepared in the following manner. Water-swollen films (obtained by soaking the polymer films for several hours for removal of occluded lithium chloride and solvent as aforescribed) were cut into strips. The strips were mounted between the jaws of a mechanical unidirectional stretcher. The strips were oriented by stretching (in air at 200°C) to an elongation in the range of 50 to 55 %. The polymeric strips were optically transparent. Birefringence, measured with the aid of a quartz wedge, was 0.35. Strips were also stretched in methanol at 25°C to an elongation of 55 %. Measurement of birefringence for such stretched films showed a birefringence of 0.44.

#### Example 6

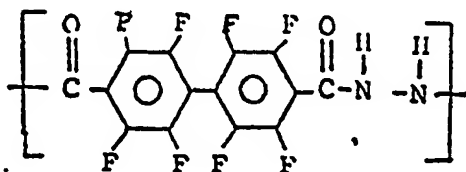
This example illustrates the preparation of poly(2,2',3,3',4,4',6,6'-octafluoro-4,4'-biphenylene) carbohydrazide and the preparation therefrom of birefringent polymeric films.

A 50-ml reaction vessel (a resin-making kettle equipped with a mechanical stirrer, nitrogen inlet tube and calcium chloride drying tube) was heated while simultaneously flushing the vessel with nitrogen. After the reaction vessel had cooled to room temperature, 1.15 g of anhydrous lithium chloride and 0.0386 g (0.001205 mole) of distilled hydrazine were added while maintaining a positive nitrogen pressure. The reaction vessel was fitted with a thermometer and a rubber stopple and 7 ml of anhydrous distilled N-methylpyrrolidone (NMP) and 12 ml of anhydrous distilled tetramethylurea (TMU) were carefully



1 added with the aid of syringes. The resulting mixture was  
 stirred until most of the lithium chloride had dissolved.  
 The solution was then cooled in a bath of ice and salt to  
 a temperature of 0°C. A small amount of lithium chloride  
 precipitation was observed. Distilled 2,2',3,3',5,5',6,6'-  
 5 octafluoro-4,4'-biphenylene dicarbonyl chloride (0.5100 g;  
 0.001205 mole) was quickly added by means of a funnel to the  
 stirred hydrazine solution. An additional 4 ml of TMU (at a  
 temperature of 25°C) were added through the funnel to the  
 reaction mixture. The temperature of the reaction mixture  
 10 did not rise above a temperature of 5°C. The reaction  
 mixture did not thicken and streaming birefringence was not  
 observed. Lithium carbonate (0.0890 g; 0.0024 mole) was  
 added to the reaction mixture, stirring was continued for  
 30 minutes at 4°C and the ice bath was removed. As the  
 15 temperature of the reaction mixture rose to 25°C during  
 the subsequent 60 minutes, the reaction solution first  
 became cloudy and, then, a white precipitate formed. Over  
 the next 30 minutes, the reaction mixture was warmed to  
 40°C at which time the reaction mixture became homogeneous.  
 20 The reaction temperature was raised to 70°C and maintained  
 for 1 hour. No increase in viscosity was apparent.

The reaction product, a 1.99 % wt./vol. polymer solution  
 (1.99 g of polymer per 100 ml of reaction solvent) was  
 25 cooled to 40°C and poured into 200 ml of ice-water in a  
 blender. The resulting powdery solid was filtered and  
 washed (in the blender) twice each with water, acetone  
 and ether. The product was dried in a vacuum oven at 15 mm  
 Hg pressure and 90°C for 18 hours. The polymeric product,  
 30 obtained in 95.4 % yield, was a white solid material having  
 the following recurring structural units:



1 The inherent viscosity of a polymer solution (0.5 g of the polymer of Example 6 per 100 ml of a solution of 5 g lithium chloride per 100 ml of dimethylacetamide) was 1.16 dl/g at 30°C. The molecular structure of the polymer of Example 6 was confirmed by infrared spectroscopy.

5 Polymeric films were prepared from the polymeric material of Example 6 by casting (onto glass plates) solutions of the polymeric material in a 2 % wt./vol. solution of lithium chloride and dimethylacetamide (2 g lithium  
10 chloride per 100 ml of dimethylacetamide). The concentration of polymer ranged from 0.5 to 5 % wt./vol., i.e., from 0.5 g to 5 g polymer per 100 ml of the lithium chloride/dimethylacetamide solution. In each instance, the glass plate carrying the puddle cast polymer solution was  
15 immersed in water (after evaporating the solvent for 1 hour). The polymer film was observed to gel, and a physically weak, cloudy and colourless film separated from the glass plate. The resulting film was soaked for several hours in water to effect extraction of occluded lithium  
20 chloride and solvent, soaked in acetone and dried in a vacuum oven at 90°C and 15 mm pressure. The films were not of sufficient strength to undergo stretching. Refractive index, measured by interferometry, was 1.60.

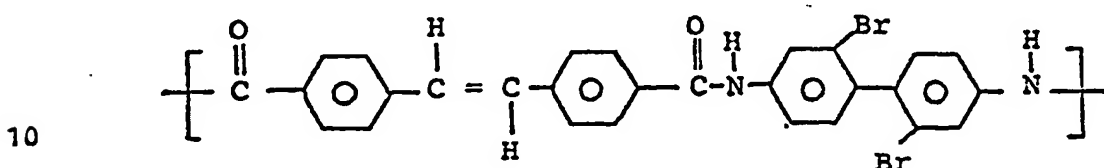
#### 25 Example 7

This example illustrates the preparation of poly(2,2'-di-bromo-4,4'-biphenylene)-trans-p,p'-stilbene dicarboxamide and the preparation therefrom of birefringent polymeric  
30 films.

A 250-ml reaction vessel (a resin-making kettle equipped with a mechanical stirrer, nitrogen inlet tube and calcium chloride drying tube) was heated while simultaneously  
35 flushing the vessel with nitrogen. After the reaction

- 1 vessel had cooled to room temperature, 4.88 g of anhydrous lithium chloride and 2.1441 g (0.006269 mole) of sublimed 2,2'-dibromobenzidine were added while maintaining a positive nitrogen pressure. The reaction vessel was fitted with a thermometer and a rubber stopple and 45 ml of anhydrous distilled N-methylpyrrolidone (NMP) and 45 ml of anhydrous distilled tetramethylurea (TMU) were carefully added with the aid of syringes. The resulting mixture was stirred and warmed to 40°C until all solids had dissolved. The solution was then cooled in a bath of ice and salt to a temperature of -5°C. A small amount of lithium chloride precipitation was observed. Recrystallized trans-p,p'-stilbene dicarbonyl chloride (1.9129 g; 0.006269 mole) was quickly added by means of a funnel to the stirred 2,2'-dibromobenzidine solution. An additional 30 ml of NMP/TMU mixture (1:1 by weight), at a temperature of 25°C, were added through the funnel to the reaction mixture. The temperature of the reaction mixture did not rise above a temperature of 5°C and then dropped rapidly to -3°C. After stirring for 30 minutes, the reaction mixture began to thicken and streaming birefringence (but not stir opalescence) was observed. Lithium carbonate (0.926 g, 0.01254 mole) was added and stirring was continued for an additional 30 minutes at 0°C.
- 25 The ice bath was removed from the reaction vessel, and when the temperature reached 20°C (in 30 minutes), the reaction solution had become sufficiently viscous as to begin to climb the shaft of the mechanical stirrer. A maximum reaction temperature of 55°C was reached. Stirring was stopped and the mixture was heated overnight at a temperature of 55°C. The reaction product, a viscous polymer solution of 3 % wt./vol. concentration (3 g of polymer per 100 ml of reaction solvent) was diluted with 130 ml of 2 % wt./vol. lithium chloride in dimethylacetamide. The resulting polymer solution was poured into 200 ml of ice

1 and water in a blender. The resulting fibrous solid was  
 filtered and washed (in the blender) twice each with water,  
 acetone and ether. The product was dried in a vacuum oven  
 at 15 mm Hg pressure and 90°C for 18 hours. The polymeric  
 product, obtained in 100 % yield, was a very light-yellow  
 5 fibrous solid having the following recurring structural  
 units:



15 The inherent viscosity of a polymer solution (0.5 g of the  
 polymer of Example 7 per 100 ml of a solution of 5 g  
 lithium chloride per 100 ml of dimethylacetamide) was 9.04  
 dl/g at 30°C. The molecular weight of the polymer, as  
 determined by light scatterings, was  $1.95 \times 10^6$ , and by  
 gel permeation chromatography,  $8.71 \times 10^5$ .

20 The molecular structure of the polymer was confirmed by  
 infrared spectroscopy. Inspection of the ultraviolet/  
 visible spectrum of the polymer (in 5 % wt./vol. lithium  
 chloride/dimethylacetamide) showed a  $\lambda_{\max}$  of 352 nm  
 ( $\epsilon = 66,000$ ); an absorption peak at 368 nm ( $\epsilon = 52,800$ )  
 25 and an extremely weak tail at 400 nm.

Elemental analysis for  $C_{28}H_{18}Br_2N_2O_2$  provided the follow-  
 ing:

30

	%C	%H	%Br	%N	%O
Calculated:	58.56	3.16	27.83	4.88	5.57
Found:	58.50	3.22	27.94	4.87	5.47 (by differ- ence)

35 Thermogravimetric analysis showed that the onset of  
 degradation of the polymer of Example 7 occurred at 470°C

1 in nitrogen and at 515°C in air. Differential scanning  
calorimetry and thermal mechanical analysis of film samples  
detected a reproducible transition at about 225°C.

Polymeric films were prepared from the polymeric material  
5 of Example 7 by casting (onto glass plates) solutions of  
the polymeric material in a 5 % wt./vol. solution of  
lithium chloride and dimethylacetamide (5 g lithium  
chloride per 100 ml of dimethylacetamide). The concentrat-  
ion of polymer ranged from 1 to 5 % wt./vol., i.e., from  
10 1 g to 5 g polymer per 100 ml of the lithium chloride/  
dimethylacetamide solution. In each instance, the glass  
plate carrying the puddle-cast polymer solution was  
immersed in water (after minimal evaporation of solvent).  
The polymer was observed to gel and a transparent and  
15 colourless unoriented film separated from the soaked glass  
plate. The resulting film was soaked for several hours  
in water to effect extraction of occluded lithium chloride  
and solvent, soaked in acetone and dried in a vacuum oven  
at 90°C and 15 mm Hg pressure. Refractive index, measured  
20 by interferometry, was 2.03.

Stretched polymeric films were prepared in the following  
manner. Water-swollen films (obtained by soaking the poly-  
mer films for several hours for removal of occluded  
25 lithium chloride and solvent as aforescribed) were cut  
into strips. The strips were mounted between the jaws of  
a mechanical unidirectional stretcher. The strips were  
stretched (in air at 220°C) to about 55 to 55 % elongation,  
to effect film orientation. The stretched films were  
30 optically transparent. Infrared dichroism indicated that  
the stretched films were less than 65 % by weight oriented;  
the modulus was  $0.27 \times 10^6$  kg/m<sup>2</sup>. Wide-angle X-ray analysis  
of the films showed crystallinity to be less than 10 % by  
weight. Birefringence, measured with the aid of a quartz  
35 wedge, was 0.589.

1 Solutions of the polymer of Example 7 in lithium chloride/  
dimethylacetamide, as aforescribed, were formed into  
extruded films by the "wet-jet" method whereby the solution  
of polymer is extruded into an aqueous coagulation bath for  
gelling of the polymer material. The resulting transparent,  
5 colourless film strips were soaked in water and cut to  
about 25.4 to 50.8 mm for testing. The partially oriented  
strips of film produced by the extrusion were further  
oriented by stretching in the manner described in the  
Examples hereof. Stretching was effected in air at a  
10 temperature of 180°C. Elongation was to the break point,  
in the range of about 40 % to 50 %. The stretched strips  
were optically transparent. Infrared dichroism indicated  
that the films were 85 % oriented. Measurement of bire-  
fringence utilizing a quartz wedge provided a birefringence  
15 value of 0.977. Measurement by resort to interferometry  
provided a value of 0.865.

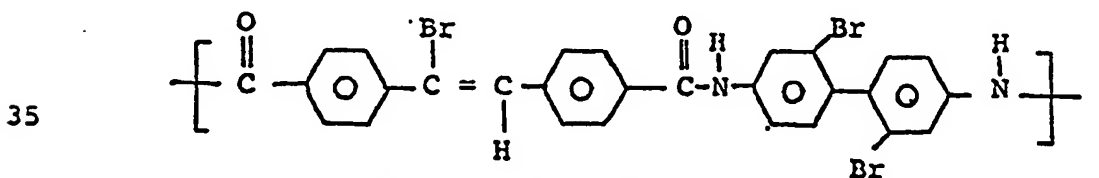
#### Example 8

20 This example illustrates the preparation of poly(2,2'-di-  
bromo-4,4'-biphenylene)-trans- $\alpha$ -bromo-biphenylene dicarb-  
oxamide and the preparation therefrom of birefringent  
polymeric films.

25 A 50-ml reaction vessel (a resin-making kettle equipped  
with a mechanical stirrer, a pressure-equalizing dropping  
funnel, a nitrogen inlet tube and calcium chloride drying  
tube) was heated while simultaneously flushing the vessel  
with nitrogen. After the reaction vessel had cooled to  
30 room temperature, 1.5 g of anhydrous lithium chloride and  
0.4779 g (0.001397 mole) of sublimed 2,2'-dibromo-benzidine  
were added while maintaining a positive nitrogen pressure.  
The reaction vessel was fitted with a thermometer and a  
rubber stopple and 15 ml of anhydrous distilled N-methyl-  
35 pyrrolidone (NMP) and 5 ml of anhydrous distilled tetra-

1 methylurea (TMU) were carefully added with the aid of  
 syringes. The resulting mixture was stirred and warmed to  
 40°C until all solids had dissolved. The solution was then  
 cooled in a bath of ice and salt to a temperature of 0°C.  
 A small amount of lithium chloride precipitation was ob-  
 5 served. Recrystallized  $\alpha$ -bromo-p,p'-stilbene dicarbonyl  
 chloride (0.5366 g; 0.001397 mole) was quickly added by  
 means of a funnel to the stirred 2,2'-dibromobenzidine  
 solution. An additional 10 ml of TMU (at a temperature of  
 25°C) were added through the funnel to the reaction mixture.  
 10 The temperature of the reaction mixture did not rise above  
 a temperature of 4°C. After stirring for 15 minutes, the  
 reaction mixture began to thicken and streaming bire-  
 fringence (but not stir opalescence) was observed. Stirring  
 was continued for an additional 30 minutes at 4°C.  
 15 The ice bath was removed from the reaction vessel and the  
 temperature was observed to rise to 25°C in 90 minutes at  
 which point the reaction mixture had become sufficiently  
 viscous as to climb the shaft of the mechanical stirrer.  
 20 Over the next 90 minutes, the very pale-yellow reaction  
 mass was gently warmed with intermittent stirring; the  
 maximum temperature reached was approximately 70°C.

The reaction product, a 3 % wt./vol. polymer solution  
 25 (3 g of polymer per 100 ml of reaction solvent) was cooled  
 to 40°C and poured into 200 ml of ice-water in a blender.  
 The resulting fibrous solid was filtered and washed (in  
 the blender) twice each with water, acetone and ether. The  
 product was dried in a vacuum oven at 15 mm Hg pressure at  
 30 90°C for 18 hours. The product, obtained in 95.4 % yield,  
 was a light-yellow fibrous polymeric material having the  
 following recurring structural units:



- 1 The inherent viscosity of a polymer solution (0.5 g of the polymer of Example 8 per 100 ml of a solution of 5 g lithium chloride per 100 ml of dimethylacetamide) was 7.81 dl/g at 30°C.
- 5 Molecular structure was confirmed by infrared spectroscopy. Elemental analysis for  $C_{28}H_{17}N_2Br_3O_2$  provided the following:

	<u>%C</u>	<u>%H</u>	<u>%Br</u>	<u>%N</u>	<u>%O</u>
Calculated:	51.478	2.604	36.724	4.289	4.90
10 Found:	51.17	2.80	34.92	4.15	7.06 (by difference)

- Polymeric films were prepared from the polymeric material of Example 8 by casting (onto glass plates) solutions of the polymeric material in a 5 % wt./vol. solution of lithium chloride and dimethylacetamide (5 g lithium chloride per 15 100 ml of dimethylacetamide). The concentration of polymer ranged from 0.5 to 5 % wt./vol., i.e., from 0.5 g to 5 g polymer per 100 ml of the lithium chloride/dimethylacetamide solution. In each instance, the glass plate carrying the 20 puddle-cast polymer solution was immersed in water (after minimal evaporation of solvent). The polymer was observed to gel and a transparent and colourless unoriented film separated from the soaked glass plate. The resulting film was soaked for several hours in water to effect extraction 25 of occluded lithium chloride and solvent, soaked in acetone and dried in a vacuum oven at 90°C and 15 mm Hg pressure. Refractive index, measured by interferometry, was 2.07.

- 30 Stretched polymeric films were prepared in the following manner. Water-swollen films (obtained by soaking the polymer films for several hours for removal of occluded lithium chloride and solvent as aforescribed) were cut into strips. The strips were mounted between the jaws of a mechanical unidirectional stretcher. The strips were 35 stretched (in air at 220°C) to about 60 % to 65 % elongation,



1 to effect film orientation. The stretched strips were optically transparent. Birefringence, measured with the aid of a quartz wedge, was 0.680.

Solutions of the polymer of Example 8 in lithium chloride/  
5 dimethylacetamide, as aforescribed, were formed into extruded films by the "wet-jet" method whereby the solution of polymer is extruded into an aqueous coagulation bath for gelling of the polymer material. The resulting transparent, colourless film strips were soaked in water and cut to  
10 about 25.4 to 50.8 mm for testing. The partially oriented strips of film produced by the extrusion were further oriented by stretching in the manner described in the Examples hereof. Stretching was effected in air (at a temperature of 180°C) to the break point, in the range of  
15 about 40 % to 50 % elongation. The stretched film strips were optically transparent. Measurement of birefringence utilizing a quartz wedge provided a birefringence value of 0.955. Measurement by resort to interferometry provided a value of 0.849.

20

#### Example 9

This example illustrates the preparation of poly(2,2'-di-bromo-4,4'-biphenylene)- $\alpha,\alpha'$ -dimethylmuconamide and the  
25 preparation therefrom of birefringent polymeric films.

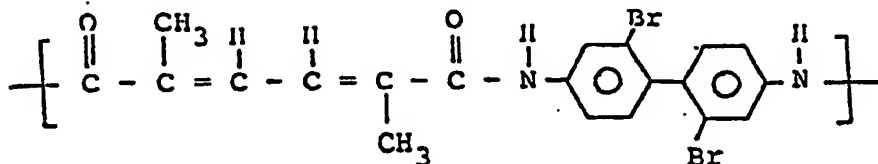
A 50-ml reaction vessel (a resin-making kettle equipped with a mechanical stirrer, a pressure-equalizing dropping funnel, a nitrogen inlet tube and calcium chloride drying tube) was  
30 heated while simultaneously flushing the vessel with nitrogen. After the reaction vessel had cooled to room temperature, 0.4 g of anhydrous lithium chloride and 0.8519 g (0.00249 mole) of sublimed 2,2'-dibromo-benzidine were added while maintaining a positive nitrogen pressure. The reaction vessel  
35 was fitted with a thermometer and a rubber stopple and 10 ml

1 of anhydrous distilled N-methylpyrrolidone (NMP) were care-  
fully added with the aid of a syringe. The resulting  
mixture was stirred and warmed to 40°C until all solids  
had dissolved. The solution was then cooled in a bath of  
ice and salt to a temperature of 0°C with formation of some  
5 lithium chloride precipitate. A solution of recrystallized  
 $\alpha,\alpha'$ -dimethyl muconyl chloride (0.5157 g; 0.002491 mole)  
in 6 ml of anhydrous, distilled tetrahydrofuran (THF) was  
added to the dropping funnel through a rubber stopper with  
a syringe. The  $\alpha,\alpha'$ -dimethyl muconyl chloride/THF solution,  
10 the temperature of which was 25°C, was added dropwise over  
5 minutes to the cold 2,2'-dibromobenzidine solution while  
stirring moderately. The addition funnel was rinsed with  
6 ml of NMP which was also added dropwise to the reaction  
mixture in order to prevent the temperature of the reaction  
15 mixture from rising above 1°C. After stirring for 1 hour,  
during which time the solution turned lemon-yellow (but did  
not thicken), 0.354 g of solid lithium carbonate was added  
all at once to the reaction mixture. Within 10 minutes  
noticeable thickening was observed, and after an additional  
20 20 minutes, at 20°C, the viscosity increased further. The  
ice bath was removed from the reaction vessel and the  
temperature of the reaction mixture was allowed to rise to  
25°C over a one-hour period during which time a thick paste  
had formed. The temperature of the reaction mixture was  
25 increased to 65°C over the next 20 minutes producing a  
mixture which could no longer be stirred. Additional heat-  
ing for 18 hours at 55°C without stirring produced a trans-  
parent, light-yellow viscous polymer solution. The reaction  
product, a 5.36 % wt./vol. polymer solution (5.6 g of poly-  
30 mer per 100 ml of reaction solvent) was observed to exhibit  
considerable streaming birefringence upon application of low  
mechanical stress; stir opalescence was not, however,  
observed.

35 The polymer solution was poured into a blender containing  
200 ml of ice-water and the resulting fibrous solid was

1 filtered and washed (in the blender) twice each with water,  
acetone and ether. The product was dried in a vacuum oven  
at 15 mm Hg pressure and 90°C for 18 hours. The product,  
obtained in 94.7 % yield, was a white fibrous polymeric  
material having the following recurring structural units:

5



10

The inherent viscosity of a polymer solution (0.5 g of the  
polymer of Example 9 per 100 ml of a solution of 5 g lithium  
chloride per 100 ml of dimethylacetamide) was 4.69 dl/g at  
30°C.

15

Molecular structure was confirmed by infrared spectrometry.  
Inspection of the ultraviolet/visible absorption spectrum  
for the polymer of Example 9 (in 3 % wt./vol. lithium  
chloride/dimethylacetamide showed a  $\lambda_{\max}$  of 333 nm ( $\epsilon =$   
20 33,600) and an extremely weak tail at 400 nm.

Elemental analysis for  $C_{20}H_{16}Br_2N_2O_2$  provided the following:

	%C	%H	%Br	%N	%O
25 <u>Calculated:</u>	50.448	3.387	33.562	5.883	6.72
<u>Found:</u>	50.09	3.45	34.17	5.72	6.57 (by
					difference.

Thermogravimetric analysis showed that the onset of  
degradation occurred at 360°C in nitrogen and at 310°C in  
30 air. Differential scanning calorimetry and thermal mechanic-  
al analysis of film samples showed a reproducible transition  
at about 185°C.

Polymeric films were prepared from the polymeric material  
35 of Example 9 by casting (onto glass plates) solutions of the

- 1 polymeric material in a 5 % wt./vol. solution of lithium  
chloride and dimethylacetamide (5 g lithium chloride per  
100 ml of dimethylacetamide). The concentration of polymer  
ranged from 2 to 4 % wt./vol., i.e., from 2 g to 4 g polymer  
per 100 ml of the lithium chloride/dimethylacetamide solut-  
5 ion. In each instance, the glass plate carrying the puddle-  
cast polymer solution was immersed in water (after minimal  
evaporation of solvent). The polymer film was observed to  
gel and a transparent and colourless unoriented film  
separated from the glass plate. The resulting film was soaked  
10 for several hours in water to effect extraction of occluded  
lithium chloride and solvent, soaked in acetone and dried in  
a vacuum oven at 90°C and 15 mm Hg pressure. Refractive  
index, measured by interferometry, was 1.91.
- 15 Stretched polymeric films were prepared in the following  
manner. Water-swollen films (obtained by soaking the poly-  
mer films for several hours for removal of occluded lithium  
chloride and solvent as aforescribed) were cut into strips.  
The strips were mounted between the jaws of a mechanical  
20 stretcher and were unidirectionally stretched, successively,  
in steam, acetone and boiling ethylene glycol (all of which  
function as plasticizers). The strips were stretched to an  
elongation of from 35 % to 45 %. The film strips were  
further elongated (up to 60%) by stretching in air at 200°C.  
25 The stretched strips were optically transparent. Optical  
retardation was measured with a calibrated quartz wedge; film  
thickness was measured with a micrometer. Birefringence,  
measured by means of a quartz wedge, was 0.40.

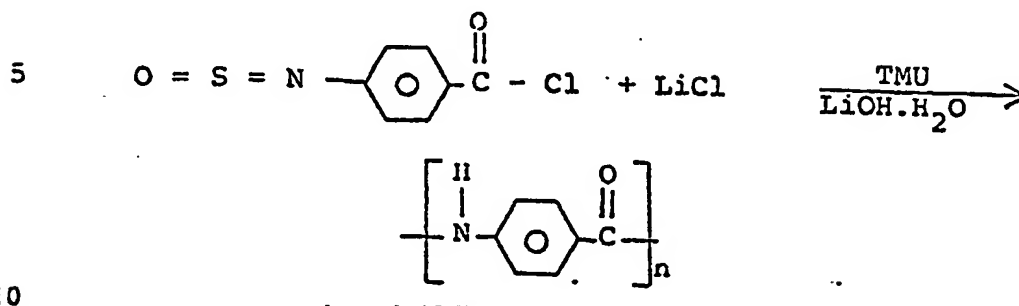
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Example 10

For purposes of comparison with the substituted polyamides  
of the present invention, an unsubstituted polyamide was  
prepared and evaluated in the following manner.

35

- 1 A solution polymerization reaction for the production of  
poly(p-benzamide) was conducted in accordance with the  
following reaction scheme:



- A 50-ml reaction vessel (a resin-making kettle equipped with mechanical stirrer, nitrogen inlet tube and calcium chloride drying tube) was heated while simultaneously  
15 flushing the vessel with nitrogen. After the reaction vessel had cooled to room temperature, 40 ml of anhydrous distilled tetramethyl urea (TMU), 8.04 g (0.04 mole) of vacuum-distilled p-thionylaminobenzoyl chloride and 0.52 g (0.012 mole) of lithium chloride were added while maintain-  
20 ing a positive nitrogen pressure. The resulting reaction mixture was stirred for ten minutes at room temperature and 1.68 g (0.04 mole) of lithium hydroxide monohydrate were added while vigorously stirring. The reaction mixture was then stirred for 1 hour at room temperature. After a period  
25 of 7 additional minutes, the reaction mixture became cloudy and was observed to thicken. The polymeric reaction product, after 20 minutes, thickened sufficiently to adhere the shaft of the mechanical stirrer. After one-half hours, the reaction mixture, which could not be stirred, was heated.  
30 An additional quantity (14 ml) of TMU was added at which point the reaction mixture still could not be stirred. The reaction mixture was then heated to 130°C without stirring. After 2 hours of heating at 130°C, pliability of polymeric reaction mass increased and the product appeared to have  
35 partially dissolved. The reaction product was stored in the

1 reaction vessel overnight and was washed with water, filtered and washed with acetone then ether. The product, poly(p-benzamide) was dried in a vacuum oven at 80°C for 2 hours.

5 The inherent viscosity of a polymer solution of poly(p-benzamide) in sulfuric acid was 1.60 dl/g at 30°C.

Polymeric films of poly(p-benzamide) were prepared by casting a solution of the polymeric material in a 5 % wt./vol. solution of lithium chloride and dimethylacetamide (5 g lithium chloride per 100 ml of dimethylacetamide). The concentration of polymer was 5 % wt./vol., i.e., 5 g polymer per 100 ml of the lithium chloride/dimethylacetamide solution. The cast polymer film was dried in a vacuum oven at 90°C overnight. The polymer film was an opaque, white flexible film. Additional films were formed by puddle-casting the solution as aforescribed onto glass plates. In each instance, the glass plate carrying the puddle-cast polymer solution was immersed in water (after most of the solvent had evaporated). The polymer film which separated from the glass plate was a tough, transparent, flexible film. The resulting film was soaked for several hours in water to effect extraction of occluded lithium chloride and solvent.

25 Stretched polymeric films were prepared in the following manner. Water-swollen films (obtained by soaking the polymer films for several hours for removal of occluded lithium chloride and solvent as aforescribed) were cut into strips. The strips were mounted between the jaws of a mechanical stretcher and were unidirectionally stretched, successively, in steam and in air (at 200°C). The strips were stretched to an elongation of approximately 10 %. The resulting stretched films were clouded in appearance.

35 Optical retardation was measured with a calibrated quartz

1 wedge; film thickness was measured with a micrometer. Birefringence, measured by means of a quartz wedge, was 0.23.

By inspection of the values of birefringence described in connection with the substituted polyamides of the present invention and the Examples hereof (Examples 1 to 9), it can be seen that the birefringence of poly(p-benzamide) of comparative Example 10, was, in general, decidedly lower.

#### Example 11

10

This example illustrates the preparation of poly-[2,2'-bis-(trifluoromethyl)-4,4'-biphenylene]-trans-p,p'-stilbene dicarboxamide and the preparation therefrom of birefringent polymeric films.

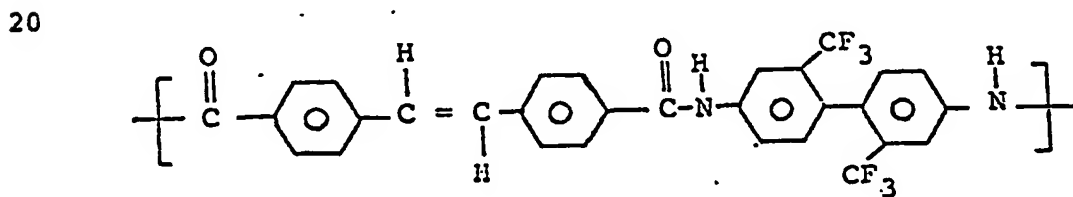
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A 100-ml reaction vessel (a resin-making kettle equipped with a mechanical stirrer, nitrogen inlet tube and calcium chloride drying tube) was heated while simultaneously flushing the vessel with nitrogen. After the reaction vessel had cooled to room temperature, 1.5 g of anhydrous lithium chloride and 0.5171 g (0.001615 mole) of recrystallized 2,2'-bis(trifluoromethyl)-benzidine were added while maintaining a positive nitrogen pressure. The reaction vessel was fitted with a thermometer and a rubber stopple and 10 ml of anhydrous distilled tetramethylurea (TMU) were carefully added with the aid of syringes. The resulting mixture was stirred and warmed to 40°C until all solids had dissolved. The solution was then cooled in a bath of ice and salt to a temperature of -5°C. A small amount of lithium chloride precipitation was observed. Recrystallized trans-p,p'-stilbene dicarbonyl chloride (0.4923 g; 0.001615 mole) was carefully added by means of a funnel to the stirred 2,2'-bis(trifluoromethyl)-benzidine solution. An additional 10 ml of TMU, at a temperature of 0°C, were added through the funnel to the reaction mixture. The temperature of the

20  
25  
30  
35

1 reaction mixture did not rise above a temperature of 5°C  
 and then dropped rapidly to -3°C. After stirring for  
 30 minutes, the reaction mixture began to thicken and  
 streaming birefringence (but not stir opalescence) was  
 observed. Stirring was continued for an additional  
 5 30 minutes at 0°C.

The ice bath was removed from the reaction vessel, and when  
 the temperature reached 20°C (in 30 minutes), the reaction  
 solution had become very viscous. Over the next 75 minutes,  
 10 the completely colourless, transparent solution was warmed  
 to 72°C. After stirring at this temperature for the next  
 18 hours, the mixture was cooled to 40°C. The resulting  
 polymer solution was poured into 200 ml of ice and water in  
 a blender. The resulting fibrous solid was filtered and  
 15 washed (in the blender) twice each with water, acetone and  
 ether. The product was dried in a vacuum oven at 15 mm Hg  
 pressure and 90°C for 18 hours. The polymeric product,  
 obtained in 99.5 % yield, was a very light-yellow fibrous  
 solid having the following recurring structural units:



25 The inherent viscosity of a polymer solution (0.5 g of the  
 polymer of Example 11 per 100 ml of a solution of 5 g  
 lithium chloride per 100 ml of dimethylacetamide) was  
 4.735 dl/g at 30°C. The molecular structure of the polymer  
 30 was confirmed by infrared spectroscopy.

Elemental analysis for  $C_{20}H_{12}F_6N_2O_2$ , provided the following:

	%C	%H	%F	%N	%O
35 Calculated:	65.22	3.28	20.64	5.07	5.79
Found:	64.54	3.76	19.04	4.85	7.81 (by difference)



1 Thermogravimetric analysis showed that the onset of degradation of the polymer of Example 11 occurred at 500°C in nitrogen and at 410°C in air. Differential scanning calorimetry and thermal mechanical analysis of film samples detected a reproducible transition at about 185°C.

5 Polymeric films were prepared from the polymeric material of Example 11 by casting (onto glass plates) solutions of the polymeric material in a 5 % wt./vol. solution of lithium chloride and dimethylacetamide (5 g lithium chloride  
10 per 100 ml of dimethylacetamide). The concentration of polymer ranged from 1.0 to 5 % wt./vol., i.e., from 1.0 g to 5 g polymer per 100 ml of the lithium chloride/dimethylacetamide solution. In each instance, the glass plate carrying the puddle-cast polymer solution was immersed in  
15 water (after minimal evaporation of solvent). The polymer film was observed to gel and a transparent and colourless unoriented film separated from the glass plate. The resulting film was soaked for several hours in water to effect extraction of occluded lithium chloride and solvent, soaked  
20 in acetone and dried in a vacuum oven at 90°C and 15 mm Hg pressure. Refractive index, measured by interferometry, was 1.997.

Stretched polymeric films were prepared in the following  
25 manner. Water-swollen films (obtained by soaking the polymer films for several hours for removal of occluded lithium chloride and solvent as aforescribed) were cut into strips. The strips were mounted between the jaws of a mechanical unidirectional stretcher. The strips were  
30 stretched (in air at 220°C) to about 60 to 65 % elongation, to effect film orientation. The stretched films were optically transparent. Birefringence, measured with the aid of a quartz wedge, was 0.537.

35 Solutions of the polymer of Example 11 in lithium chloride/

1 dimethylacetamide, as aforescribed, were formed into  
extruded films by the "wet-jet" method whereby the solution  
of polymer is extruded into an aqueous coagulation bath  
for gelling of the polymer material. The resulting trans-  
parent, colourless film strips were soaked in water and  
5 cut to about 25.4 to 50.8 mm for testing. The partially  
oriented strips of film produced by the extrusion were  
further oriented by stretching in the manner described in  
the Examples hereof. Stretching was effected to an elong-  
ation of less than 20 %. The stretched strips were  
10 optically transparent. Infrared dichroism indicated that  
the films were 92 % oriented. Measurement of birefringence  
utilizing a quartz wedge provided a birefringence value of  
0.879.

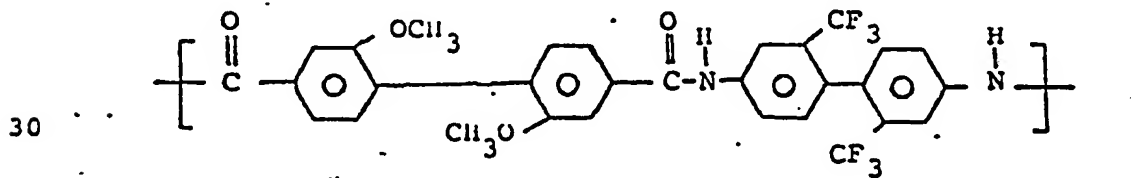
15 Example 12

This example illustrates the preparation of poly-[2,2'-bis-  
(trifluoromethyl)-4,4'-biphenylene]-2,2'-dimethoxy-4,4'-bi-  
phenyl and the preparation therefrom of birefringent poly-  
20 meric films.

A 100-ml reaction vessel (a resin-making kettle equipped  
with a mechanical stirrer, a pressure-equalizing dropping  
funnel, a nitrogen inlet tube and calcium chloride drying  
25 tube) was heated while simultaneously flushing the vessel  
with nitrogen. After the reaction vessel had cooled to room  
temperature, 3.0 g of anhydrous lithium chloride and  
0.4328 g (0.001352 mole) of recrystallized 2,2'-bis(tri-  
fluoromethyl)benzidine were added while maintaining a  
30 positive nitrogen pressure. The reaction vessel was fitted  
with a thermometer and a rubber stopple and 20 ml of an-  
hydrous distilled N-methylpyrrolidinone (NMP) and 20 ml of  
anhydrous distilled tetramethylurea (TMU) were carefully  
added with the aid of syringes. The resulting mixture was  
35 stirred and warmed to 40°C until all solids had dissolved.

1 The solution was then cooled in a bath of ice and salt to a temperature of  $-5^{\circ}\text{C}$ . A small amount of lithium chloride precipitation was observed. Recrystallized 2,2'-dimethoxy-4,4'-biphenyldicarbonyl chloride (0.4586 g; 0.001352 mole) was quickly added by means of a funnel to the stirred  
 5 2,2'-bis(trifluoromethyl)-benzidine solution. An additional 20 ml of TMU (at a temperature of  $0^{\circ}\text{C}$ ) were added through the funnel to the reaction mixture. The temperature of the reaction mixture did not rise above a temperature of  $5^{\circ}\text{C}$ . After stirring for 30 minutes, the reaction mixture began  
 10 to thicken and turned milk-like in appearance. Stirring was continued for an additional 30 minutes at  $0^{\circ}\text{C}$ .

The ice bath was removed from the reaction vessel and the temperature was observed to rise to  $20^{\circ}\text{C}$  in 30 minutes at  
 15 which point the reaction mixture was viscous and opaque. Over the next 75 minutes, the opaque reaction mass was gently warmed to  $40^{\circ}\text{C}$  at which point it became transparent. After stirring at this temperature for the next 18 hours, the reaction mixture was cooled to  $30^{\circ}\text{C}$  and poured into  
 20 400 ml of ice-water in a blender. The resulting fibrous solid was filtered and washed (in the blender) twice each with water and ether. The product was dried in a vacuum oven at 15 mm Hg pressure and  $90^{\circ}\text{C}$  for 18 hours. The product, obtained in 99.3 % yield, was an off-white fibrous polymeric  
 25 material exhibiting solubility in acetone or tetrahydrofuran and having the following recurring structural units:



The inherent viscosity of a polymer solution (0.5 g of the polymer of Example 12 per 100 ml of a solution of 5 g  
 35 lithium chloride per 100 ml of dimethylacetamide) was 1.69 dl/g at  $30^{\circ}\text{C}$ .

1 Molecular structure was confirmed by infrared spectroscopy. Inspection of the ultraviolet visible spectrum of the polymer (in 5 % wt./vol. lithium chloride/dimethylformamide) showed a  $\lambda_{\text{max}}$  of 316 nm ( $\epsilon = 2.59 \times 10^3$ ).

5 Elemental analysis for  $\text{C}_{30}\text{H}_{20}\text{F}_6\text{N}_2\text{O}_4$  provided the following:

	%C	%H	%F	%N	%O
Calculated:	61.34	3.43	19.41	4.77	10.89
Found:	59.82	3.51	18.70	4.62	13.35 (by difference)

10

Thermogravimetric analysis showed that the onset of degradation of the polymer of Example 12 occurred at 470°C in nitrogen and at 440°C in air. Differential scanning colorimetry detected a reproducible transition at about 180°C.

15

Polymeric films were prepared from the polymeric material of Example 12 by casting (onto glass plates) solutions of the polymeric material in a 5 % wt./vol. solution of lithium chloride and dimethylacetamide (5g lithium chloride per 100 ml of dimethylacetamide). The concentration of polymer ranged from 1 % to 5 % wt./vol., i.e., from 1.0 g to 5 g polymer per 100 ml of the lithium chloride/dimethylacetamide solution. In each instance, the glass plate carrying the puddle-cast polymer solution was immersed in water (after minimal evaporation of solvent). The polymer was observed to gel and a transparent and colourless unoriented film separated from the soaked glass plate. The resulting film was soaked for several hours in water to effect extraction of occluded lithium chloride and solvent, soaked in acetone and dried in a vacuum oven at 90°C and 15 mm Hg pressure. Refractive index, measured by interferometry, was 1.73.

Solutions of the polymer of Example 12 in lithium chloride/dimethylacetamide, as aforescribed, were formed into

35

1 extruded films by the "wet-jet" method whereby the solution  
of polymer is extruded into an aqueous coagulation bath for  
gelling of the polymer material. The resulting transparent,  
colourless film strips were soaked in water and cut to  
about 25.4 to 50.8 mm for testing. The partially oriented  
5 strips of film produced by the extrusion were further  
oriented by stretching in the manner described in the  
Examples hereof. Stretching was effected in air (at a  
temperature of 180°C) to an elongation of less than 20 %.  
The stretched film strips were optically transparent. Infra-  
10 red dichroism indicated that the films were 92 % oriented.  
Measurement of birefringence utilizing a quartz wedge pro-  
vided a birefringence value of 0.586.

#### Example 13

15 This example illustrates the preparation of poly[2,2',3",2"-  
2''-tetrakis(trifluoromethyl)-1,1':4',1":4",1":4'-  
quaterphenylene]-trans-p,p'-stilbenedicarboxamide and the  
preparation therefrom of birefringent polymeric films.

20 A 100-ml reaction vessel (a resin-making kettle equipped  
with a mechanical stirrer, nitrogen inlet tube and calcium  
chloride drying tube) was heated while simultaneously  
flushing the vessel with nitrogen. After the reaction vessel  
25 had cooled to room temperature, 1.5 g of anhydrous lithium  
chloride and 0.5806 g (0.0009543 mole) of recrystallized  
4,4''-diamino-2,2',3",2''-tetrakis(trifluoromethyl)-1,1':4'-  
1":4",1"-quaterphenyl were added while maintaining a  
positive nitrogen pressure. The reaction vessel was fitted  
30 with a thermometer and a rubber stopple and 10 ml of an-  
hydrous distilled N-methylpyrrolidone (NMP) and 10 ml of  
anhydrous distilled tetramethylurea (TMU) were carefully  
added with the aid of syringes. The resulting mixture was  
stirred and warmed to 40°C until all solids had dissolved.  
35 The solution was then cooled in a bath of ice and salt to a

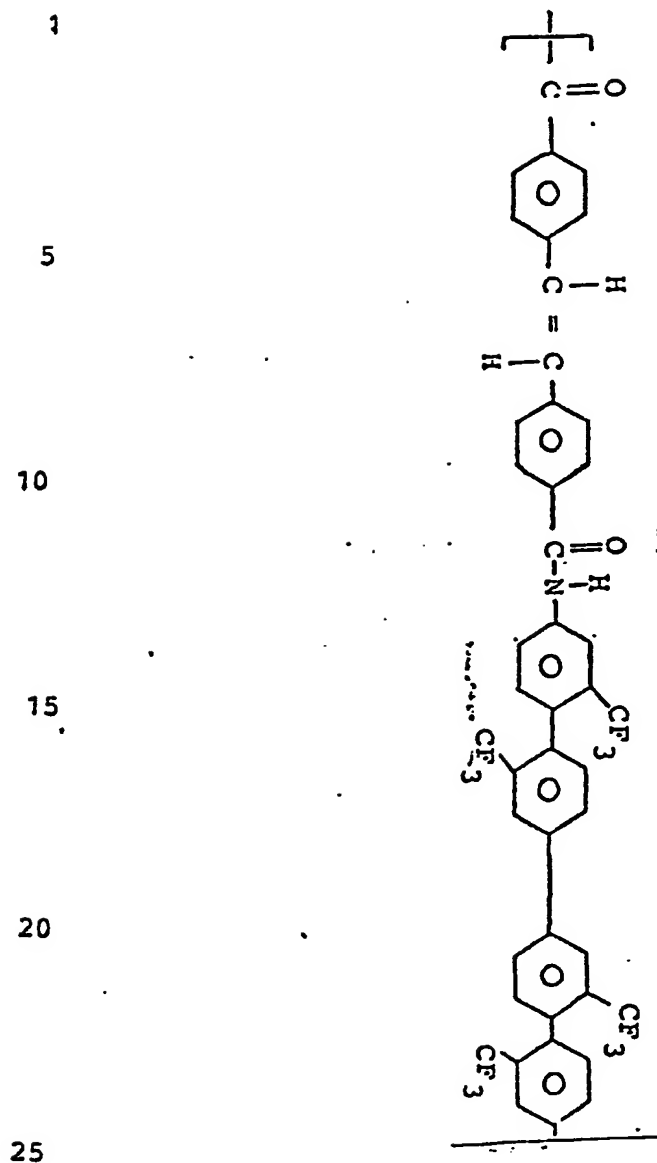
1 temperature of  $-5^{\circ}\text{C}$ . A small amount of lithium chloride  
precipitation was observed. Recrystallized trans-p,p'-  
stilbene dicarbonyl chloride (0.2909 g; 0.0009543 mole) was  
carefully added by means of a funnel to the stirred diamino-  
5 quaterphenyl solution. An additional 10 ml of TMU, at a  
temperature of  $0^{\circ}\text{C}$ , were added through the funnel to the  
reaction mixture. The temperature of the reaction mixture  
did not rise above a temperature of  $7^{\circ}\text{C}$  and then dropped  
rapidly to  $0^{\circ}\text{C}$ . After stirring for 30 minutes, the reaction  
10 mixture began to thicken and streaming birefringence (but  
not stir opalescence) was observed. Stirring was continued  
for an additional 30 minutes  $0^{\circ}\text{C}$ .

The ice bath was removed from the reaction vessel, and when  
the temperature reached  $20^{\circ}\text{C}$  (in 30 minutes), the reaction  
15 solution had become very viscous. Over the next 75 minutes,  
the light yellow, opaque solution was warmed to  $45^{\circ}\text{C}$ . After  
stirring at this temperature for the next 18 hours, the  
transparent polymer solution was poured into 200 ml of ice  
and water in a blender. The resulting fibrous solid was  
20 filtered and washed (in the blender) twice each with water  
and ether. The product was dried in a vacuum oven at 15 mm  
Hg pressure and  $90^{\circ}\text{C}$  for 18 hours. The polymeric product,  
obtained in 92.2 % yield, was a very light-yellow fibrous  
solid having the following recurring structural units:

25

30

35



The inherent viscosity of a polymer solution (0.5 g of the polymer of Example 13 per 100 ml of a solution of 5 g lithium chloride per 100 ml of dimethylacetamide) was 1.31 dl/g at 30°C. The molecular structure of the polymer was confirmed by infrared spectroscopy. The polymer was soluble in tetrahydrofuran, in acetone and in various amide-type solvent, with and without added lithium chloride.

Elemental analysis for  $C_{44}H_{24}F_{12}N_2O_2$  provided the following:

	<u>%C</u>	<u>%H</u>	<u>%F</u>	<u>%N</u>	<u>%O</u>	
Calculated:	62.86	2.88	27.12	3.33	3.81	
Found:	62.07	3.29	24.18	3.16	7.3	(by difference)

Thermogravimetric analysis showed that the onset of degradation of the polymer of Example 13 occurred at 510°C in nitrogen and at 440°C in air. Differential scanning calorimetry and thermal mechanical analysis of film samples detected a reproducible transition at about 187°C.

Polymeric films were prepared from the polymeric material of Example 13 by casting (onto glass plates) solutions of the polymeric material in a 5 % wt./vol. solution of lithium chloride and dimethylacetamide (5 g lithium chloride per 100 ml of dimethylacetamide). The concentration of polymer ranged from 0.5 to 5 % wt./vol., i.e., from 0.5 g to 5 g polymer per 100 ml of the lithium chloride/dimethylacetamide solution. In each instance, the glass plate carrying the puddle-cast polymer solution was immersed in water (after minimal evaporation of solvent). The polymer film was observed to gel and a transparent and colourless unoriented film separated from the glass plate. The resulting film was soaked for several hours in water to effect extraction of occluded lithium chloride and solvent, soaked in acetone and dried in a vacuum oven at 90°C and 15 mm Hg pressure. Refractive index, measured by interferometry, was 1.810.

Stretched polymeric films were prepared in the following manner. Water-swollen films (obtained by soaking the polymer films for several hours for removal of occluded lithium chloride and solvent as aforescribed) were cut into strips. The strips were mounted between the jaws of a mechanical unidirectional stretcher. The strips were stretched in methanol and then in air at 220°C to effect film orientation. The stretched films were optically transparent. Bire-

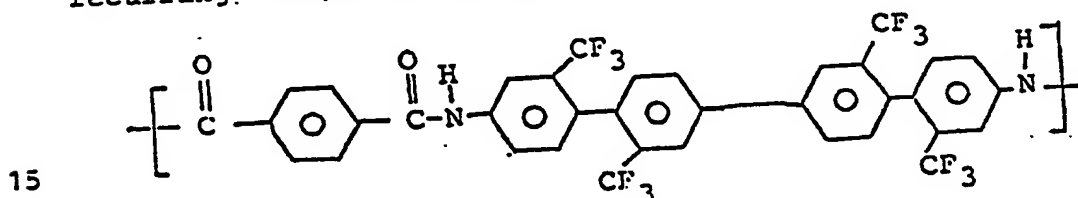


- 1 fringence, measured with the aid of a quartz wedge, was  
0.87.

Example 14

- 5 This example illustrates the preparation of poly-[2,2',3",  
2"-tetrakis(trifluoromethyl)-1,1':4', 1":4", 1"-4"-  
quaterphenylene] terephthalamide and the preparation there-  
from of birefringent polymeric films.
- 10 A 100 ml reaction vessel (a resin-making kettle equipped  
with a mechanical stirrer, nitrogen inlet tube and calcium  
chloride drying tube) was heated while simultaneously  
flushing the vessel with nitrogen. After the reaction  
vessel had cooled to room temperature, 1.5 g of anhydrous  
15 lithium chloride and 0.6301 g (0.001036 mole) of recrystall-  
ized 4,4"-diamino-2,2',3",2"-tetrakis(trifluoromethyl)-  
1,1':4',1";4",1"-quaterphenyl were added while maintaining  
a positive nitrogen pressure. The reaction vessel was fitted  
with a thermometer and a rubber stopple and 10 ml of an-  
20 hydrous distilled N-methylpyrrolidone (NMP) and 10 ml of  
anhydrous distilled tetramethylurea (TMU) were carefully  
added with the aid of syringes. The resulting mixture was  
stirred and warmed to 40°C until all solids had dissolved.  
The solution was then cooled in a bath of ice and salt to a  
25 temperature of +5°C. A small amount of lithium chloride  
precipitation was observed. Recrystallized terephthaloyl-  
chloride (0.2103 g; 0.001036 mole) was carefully added by  
means of a funnel to the stirred 2,2'-diaminoquaterphenyl  
solution. An additional 10 ml of TMU, at a temperature of  
30 10°C, were added through the funnel to the reaction mixture.  
The temperature of the reaction mixture did not rise above  
a temperature of 15°C and then dropped to 10°C. After  
stirring for 30 minutes, the reaction mixture began to  
thicken and streaming birefringence (but not stir  
35 opalescence) was observed. Stirring was continued for an  
additional 30 minutes at 10°C.

- 1 The ice bath was removed from the reaction vessel, and when the temperature reached 27°C (in 30 minutes), the reaction solution had become very viscous. Over the next 75 minutes, the light yellow, transparent solution was warmed to 40°C. After stirring at this temperature for the next 18 hours, the polymer solution was poured into 200 ml of ice and water in a blender. The resulting fibrous solid was filtered and washed (in the blender) twice each with water and ether. The product was dried in a vacuum oven at 15 mm Hg pressure and 90°C for 18 hours. The polymeric product, obtained in 93.5 % yield, was a white fibrous solid having the following recurring structural units:



- The inherent viscosity of a polymer solution (0.5 g of the polymer of Example 14 per 100 ml of a solution of 5 g lithium chloride per 100 ml of dimethylacetamide) was 6.55 dl/g at 30°C. The molecular structure of the polymer was confirmed by infrared spectroscopy. The polymer was very slightly soluble in acetone, in tetrahydrofuran and in ethyl acetate and was soluble in amide-type solvents with or without added lithium chloride.

Elemental analysis for  $C_{36}H_{18}F_{12}N_2O_2$  provided the following:

	%C	%H	%F	%N	%O	
30	Calculated:	58.23	2.44	30.71	3.77	4.85
	Found:	57.87	2.50	30.56	3.77	5.3
						(by difference)

- Thermogravimetric analysis showed that the onset of degradation of the polymer of Example 14 occurred at 440°C in nitrogen and in air. Differential scanning calorimetry and

- 1 thermal mechanical analysis of film samples detected a  
reproducible transition at about 160°C.

Polymeric films were prepared from the polymeric material  
of Example 13 by casting (onto glass plates) solutions of  
5 the polymeric material in a 5 % wt./vol. solution of  
lithium chloride and dimethylacetamide (5 g lithium  
chloride per 100 ml of dimethylacetamide). The concentrat-  
ion of polymer ranged from 0.5 to 5 % wt./vol., i.e. from  
0.5 g to 5 g polymer per 100 ml of the lithium chloride/di-  
10 methylacetamide solution. In each instance, the glass plate  
carrying the puddle-cast polymer solution was immersed in  
water (after minimal evaporation of solvent). The polymer  
film was observed to gel and a transparent and colourless  
unoriented film separated from the glass plate. The result-  
15 ing film was soaked for several hours in water to effect  
extraction of occluded lithium chloride and solvent, soaked  
in acetone and dried in a vacuum oven at 90°C and 15 mm Hg  
pressure. Refractive index, measured by interferometry,  
was 1.79.

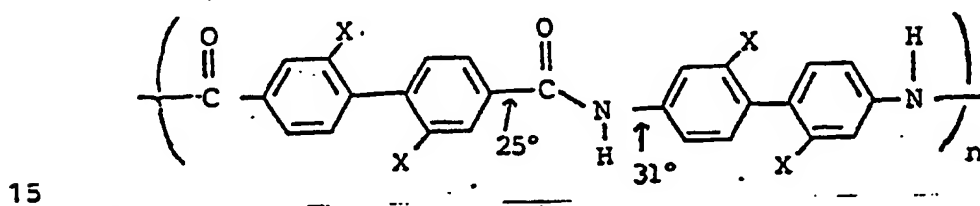
20 Stretched polymeric films were prepared in the following  
manner. Water-swollen films (obtained by soaking the poly-  
mer films for several hours for removal of occluded lithium  
chloride and solvent as aforescribed) were cut into  
25 strips. The strips were mounted between the jaws of a  
mechanical unidirectional stretcher. The strips were  
stretched (in air at 220°C) to effect film orientation. The  
stretched films were optically transparent. Birefringence,  
measured with the aid of a quartz wedge, was 0.293.

30 Solutions of the polymer of Example 14 in lithium chloride/  
dimethylacetamide, as aforescribed, were formed into  
extruded films by the "wet-jet" method whereby the solution  
of polymer is extruded into an aqueous coagulation bath for  
35 gelling of the polymer material. The resulting transparent

1 colourless film strips were soaked in water and cut to  
 about 25.4 to 50.8 mm for testing. The partially oriented  
 strips of film produced by the extrusion were further  
 oriented by stretching in the manner described in the  
 Examples hereof. Measurement of birefringence utilizing a  
 5 quartz wedge provided a birefringence value of 0.44.

#### Example 15

10 Geometric indices were determined for the repeating units of  
 polymeric materials having the following structure



wherein each X is hydrogen or a substituent as set forth in  
 the following Table I. In the case of each recurring unit,  
 the eccentricity factor  $\frac{1 + e_L}{1 + e_T}$  was calculated and is report-  
 20 ed in Table I. Bond and group<sup>T</sup> polarizability tensors were  
 utilized to calculate a polarizability matrix for each  
 repeat unit, the diagonalized form of the matrix providing  
 the X, Y and Z contributions to the unit polarizability  
 ellipsoid. Axial polarizabilities, i.e., X, Y and Z, were  
 25 utilized to calculate longitudinal and transverse  
 eccentricities of each repeat unit, thus, reflecting its  
 symmetry.

30 Eccentricity values were calculated utilizing the following  
 procedure. A polarizability and a corresponding orthogonal  
 coordinate system is assigned to each segment of the poly-  
 mer repeat unit. Literature values for group polarizabil-  
 ities are utilized from the literature, or where not avail-  
 able, are constructed from bond polarizabilities. Available  
 35 Denbigh values were utilized herein for all calculations.

1 Bond polarizabilities are utilized to connect segments  
where necessary. To determine the overall polarizability  
of the repeat unit, the coordinate system of the segment at  
one end of the repeat unit is made coincident with that of  
the adjacent segment by means of the appropriate rotation(s).  
5 This procedure is repeated on each successive  
segment until the last segment is reached. Mathematically,  
this means that the matrix of one segment must be pre- and  
post-multiplied by a transformation matrix:

10 
$$\alpha_1' = \underline{T} \alpha_1 \underline{T}^{-1}$$

where  $\alpha_1$  is the polarizability of segment 1;  $\underline{T}$  is the  
transformation matrix;  $\underline{T}^{-1}$  is the inverse of  $\underline{T}$ ; and  $\alpha_1'$  is  
the polarizability of segment 1 in the coordinate system of  
segment 2. The value of  $\alpha_1'$  is then added to  $\alpha_2$  and the  
15 transformation repeated. The repeat unit polarizability  
matrix is diagonalized, thus, providing a repeat unit  
polarizability ellipsoid with three semi-axes, i.e.,  $\alpha_{xx}$ ,  
 $\alpha_{yy}$ , and  $\alpha_{zz}$ , where  $\alpha_{xx}$  is the major polarizability and  
20 is coincident with the polymer backbone.

Literature-reported values of 25° and 31°, respectively,  
were utilized in all calculations as representing the di-  
hedral angle between the phenyl and carbonyl moieties and  
the dihedral angle between the phenyl and amino moieties,  
25 respectively. Experimentally determined values for the di-  
hedral angle between each X-substituted phenyl moiety were  
utilized in all calculations and are reported in Table I.  
Mean diameter values, D, and length, L, were obtained from  
30 spacefilling molecular models.

TABLE I

	Substituent X (Dihedral Angle)	Mean Diameter (D)	Length (L)	$\left(\frac{1 + e_L}{1 + e_T}\right)$	G
1	H (20°)	4.49	21.35	1.061	0.989
5	F (60°)	4.61	21.35	1.206	1.21
	Cl (72°)	4.78	21.35	1.348	1.23
10	Br (75°)	4.83	21.35	1.388	1.24
	I (85°)	4.91	21.35	1.428	1.26
	CF <sub>3</sub> (80°)	4.90	21.35	1.496	1.33
15	CH <sub>3</sub> (71°)	4.76	21.35	1.330	1.25

From the data presented in Table I will be observed the influence of the nature of the X substituent relative to a hydrogen atom as regards the reported dihedral angle and resulting substantial noncoplanarity between interbonded phenyl rings. Differences in mean diameter and influence of the nature of X substituents on mean diameter and eccentricity factor, and correspondingly, geometric index G will also be observed. Thus, it will be noted that the largest substituents, i.e., -CF<sub>3</sub> and -I substituents, corresponded with the largest dihedral angles between interbonded phenyl groups or the highest non-coplanarity and, accordingly, recurring units having such substituents show high geometric index values:

For purposes of comparison, geometric index G was calculated for the repeat unit of poly(p-phenylene)terephthalamide having the following structure and the results thereof are

1 reported in Table II. Dihedral angle values of  $25^\circ$  and  $31^\circ$  were utilized for purposes of calculation as in the case of the repeat units of Example 15.

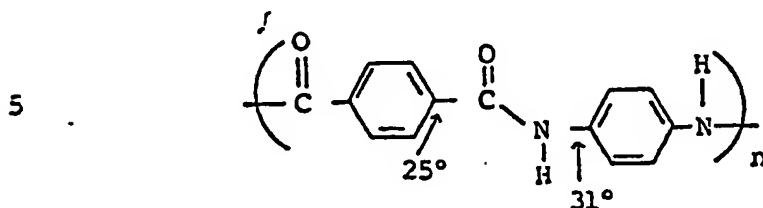


TABLE II

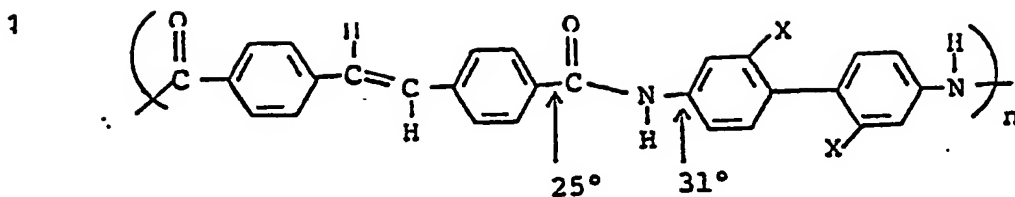
10

Mean Diameter (D)	Length (L)	$\frac{1 + e_L}{1 + e_T}$	G
4.43	12.45	0.978	0.621

15 As can be observed from inspection of the data reported in Tables I and II, the geometric indices for the repeat units of zhr materials set forth in Table I are considerably higher than the geometric index calculated for poly(p-phenylene)terephthalamide of Table II.

20 Example 16

Geometric indices for the recurring units of polyamides having the following structure were calculated. Each X substituent was as indicated in Table III. Dihedral angles from the literature were utilized in such calculations. Calculated geometric indices were compared with values of theoretical maximum birefringence for the polymeric materials, reported in Table III. Theoretical maximum birefringence values ( $\Delta n_{\max}$ ) were obtained by plotting the orientation function, calculated from infrared dichroism, against experimental birefringence and extrapolating to 100 % orientation. The results are set forth in Table III.



5

TABLE III

Substituent X (Dihedral Angle)	G	$\Delta n_{\max}$
-Br (75°)	1.21	1.20
-CF <sub>3</sub> (80°)	1.18	0.98

10

15 From the data presented in Table III, it will be seen that high values of geometric index G corresponded with high values of  $\Delta n_{\max}$ . For purposes of comparison, the theoretical maximum birefringence value ( $\Delta n_{\max}$ ) for the recurring unit of poly(p-phenylene)terephthalamide (having a G value of

20 0.621 as shown in Table II) was also determined. The resulting  $\Delta n_{\max}$  value of 0.83 for poly(p-phenylene)terephthalamide was higher than would be predicted from the geometric index value, G, of 0.621. This is believed to be the result of the highly crystalline nature of the poly(p-phenylene)tereph-

25 thalamide material, whereas the geometric index G reflects the inherent anisotropy of an isolated chain independent of such macroscopic properties as morphology, density, colour or the like.

30 The enhanced optical anisotropy exhibited by the preferred substituted-aromatic polyamide materials utilized in the optical devices hereof is believed to be the result of the rigid, rod-like uniaxial molecular structure of such materials and the amorphous/crystalline ratio thereof.

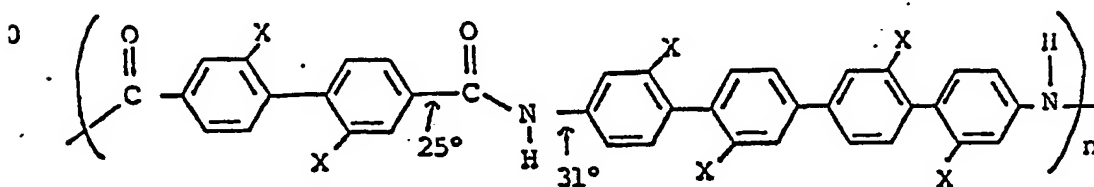
35 This ratio typically ranges from about 10:1 to about 20:1.



In the case of highly unidirectionally oriented phenyl-type polyamides this ratio generally will be in the range of about 0.3:1. The presence of crystallites is generally detrimental in polymeric materials adapted to utilization in optical devices owing to light scattering and diminished transparency. The non-coplanarity between substituted biphenyl rings, resulting from sterically bulky groups on the ortho positions of interbonded phenyl rings, raises the amorphous/crystalline ratio to a range of about 10:1 to about 20:1. This permits the fabrication of highly oriented films and fibres exhibiting high transparency in addition to high birefringence. The ring-substituted biphenyl polyamides additionally exhibit enhanced solubility and can be fabricated into colourless films or fibres where desired.

#### Example 17

Geometric indices were determined for the repeating units of polymeric materials having the following structure



wherein each X is hydrogen or a substituent as set forth in the following Table IV. In the case of each recurring unit, the eccentricity factor  $\frac{1 + e_L}{1 + e_T}$  was calculated and is reported in Table IV. Bond and group polarizability matrix for each repeat unit, the diagonalized form of the matrix providing the X, Y and Z contributions to the unit polarizability ellipsoid. Axial polarizabilities, i.e., X, Y and Z, were utilized to calculate longitudinal and transverse eccentricities of each repeat unit, thus, reflecting its symmetry.

- 1 Eccentricity values were calculated utilizing the procedure  
set forth in Example 15.

Literature-reported values of 25° and 31°, respectively,  
were utilized in all calculations as representing the di-  
5 hedral angle between the phenyl and carbonyl moieties and  
the dihedral angle between the phenyl and amino moieties,  
respectively. Experimentally determined values for the di-  
hedral angle between each X-substituted phenyl moiety were  
utilized in all calculations and are reported in Table IV.  
10 Mean diameter values, D, and length, L, were obtained from  
space-filling molecular models.

Table IV					
	Substituent X (Dihedral Angle)	Mean Diameter (D)	Length (L)	$\left(\frac{1 + e_L}{1 + c_T}\right)$	G
15	H (20°)	4.52	29.80	0.938	1.373
	F (60°)	4.66	29.80	1.155	1.640
20	Cl (72°)	4.84	29.80	1.166	1.594
	Br (75°)	4.90	29.80	1.145	1.546
25	I (85°)	4.99	29.80	1.271	1.685
	CF <sub>3</sub> (80°)	4.98	29.80	1.286	1.708
30	CH <sub>3</sub> (71°)	4.82	29.80	1.181	1.621

From the data presented in Table IV will be observed the  
influence of the nature of the X substituent relative to a  
hydrogen atom as regards the reported dihedral angle and  
35 resulting substantial noncoplanarity between interbonded

1 phenyl rings. Differences in mean diameter and influence of  
the nature of X substituents on mean diameter and  
eccentricity factor, and correspondingly, geometric index G  
will also be observed. Thus, it will be noted that the  
largest substituents, i.e., -CF<sub>3</sub> and -I substituents,  
5 corresponded with the largest dihedral angles between  
interbonded phenyl groups or the highest non-coplanarity  
and, accordingly, recurring units having such substituents  
show high geometric index values.

10 Example 18

A light-polarizing device utilizing a highly birefringent  
polyamide material was constructed in the following manner.

15 A sheet of birefringent material was prepared from the  
polyamide of Example 11, i.e., poly[2,2'-bis(trifluoro-  
methyl)-4,4'-biphenylene]-trans-p,p'-stilbene dicarboxamide.  
The sheet was prepared by the "wet-jet" extrusion method  
described in Example 11. The resulting extruded polymer, in  
20 the form of a partially oriented transparent colourless  
film, was soaked in water and cut into strips. The strips  
were then further oriented by stretching in air in the manner  
also described in Example 11. A strip of the birefringent  
polymer (having perpendicular and parallel indices of  
25 refraction, respectively, of approximately 1.72 and 2.34  
and an approximate thickness of 25μm) was embossed by con-  
tacting one surface of the strip with a brass prismatic  
plate heated to a temperature of 180°C. and pressing the  
heated plate onto the surface of the film so as to provide  
30 a prismatic layer of birefringent material generally shown  
in Fig. 6 as layer 42.

Onto a sheet of transparent isotropic glass material of  
approximately 1-mm thickness was poured a layer of poly-  
35 chlorinated biphenyl, an isotropic material having an index

1 of refraction of 1.654, available as Aroclor 1260 <sup>(R)</sup> from  
Monsanto Company, St. Louis, Missouri. The prismatic layer  
of birefringent material, prepared as aforesaid, was  
placed onto the layer of Aroclor. The prismatic layer was  
covered with a second layer of Aroclor so as to embed the  
5 prismatic layer in Aroclor material. A second sheet of  
glass was placed onto the Aroclor so as to sandwich the  
birefringent and Aroclor materials between the two pieces  
of glass. The resulting polarizer device was tested for  
its light polarizing properties by placing the test device  
10 and a second polarizer into the path of a light beam and by  
observing the attenuation of light resulting from rotation  
of the respective polarizers.

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## Claims

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1. An optical device including a transparent molecularly oriented highly birefringent polymer, said highly birefringent polymer comprising repeating molecular units exhibiting high electron density substantially cylindrically distributed about the long axes of the polymer and the repeating units thereof, said highly birefringent polymer being substantially optically uniaxial exhibiting only two indices of refraction.

10

2. A device according to claim 1 wherein the birefringence of said polymer is in relation to the molecular configuration of said repeating molecular units and the cylindrical or ellipsoidal electron density distribution about said exes according to a dimensionless geometric index G represented by the relationship

$$G = 0.222 \times E \times \frac{L}{D}$$

wherein E is a dimensionless eccentricity factor defined by the relationship

$$E = \frac{1 + e_L}{1 + e_T}$$

25

where  $e_L$  is the longitudinal eccentricity of the electron polarizability of the repeating molecular unit and  $e_T$  is the transverse eccentricity of the polarizability of the repeating molecular unit, L is the length of the repeating molecular unit along the main axis thereof and D is the mean diameter of the repeating molecular unit and wherein said geometric index G has a value of about 0.5 or higher.

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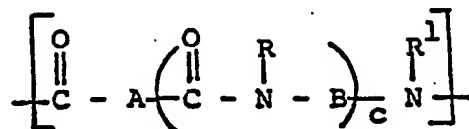
3. A device according to claim 2 wherein said geometric index G has a value of at least one, preferably at least 1.2.

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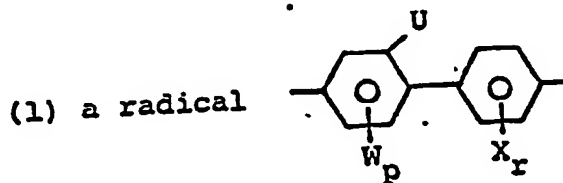
1 4. A device according to any preceding claim wherein said  
molecularly oriented highly birefringent polymer has a bi-  
refrindex of at least 0.2, preferably at least 0.4.

5 5. A device according to any preceding claim wherein said  
molecularly oriented highly birefringent polymer is in the  
form of a unidirectionally stretched polymer layer.

6. A device according to claim 1 wherein said molecularly  
oriented highly birefringent polymer comprises recurring  
10 units of the formula

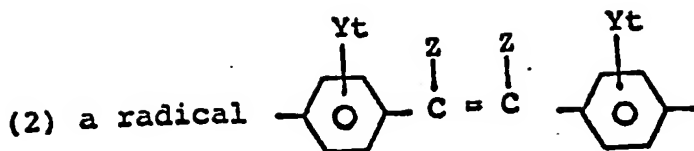


15 wherein each of A and B is a divalent radical except that B  
can additionally represent a single bond; R and R<sup>1</sup> are  
each hydrogen, alkyl, aryl, alkaryl or aralkyl; and c is  
zero or one; and wherein, when c is one, at least one of  
20 A and B is a divalent radical selected from the group con-  
sisting of:



25 where U is a substituent other than hydrogen, each W is  
hydrogen or a substituent other than hydrogen, p is an  
integer from 1 to 3, X is hydrogen or a substituent other  
30 than hydrogen and r is an integer from 1 to 4, said U, W<sub>p</sub>  
and X<sub>r</sub> substitution being sufficient to provide said  
radical with a non-coplanar molecular configuration; and

- 3 -



5 where each of Y and Z is hydrogen or a substituent other than hydrogen and each t is an integer from 1 to 4, with the proviso that when each said Z is hydrogen, at least one said Y substituent is a substituent other than hydrogen positioned on the corresponding nucleus ortho with respect

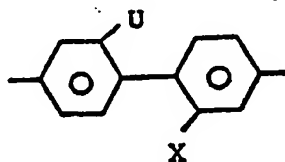
10 to the  $\overset{\text{Z}}{\underset{|}{\text{C}}}=$  moiety of said radical, said Z and Yt substitution being sufficient to provide said radical with a non-coplanar molecular configuration;

and wherein, when c is zero, A is a divalent radical selected from the group consisting of radicals (1) and (2) as

15 hereinbefore defined.

7. A device according to claim 6 wherein c of said recurring units is the integer one.

20 8. A device according to claims 6 or 7 wherein each said radical (1) is a divalent radical having the formula



wherein each of U and X is a substituent other than

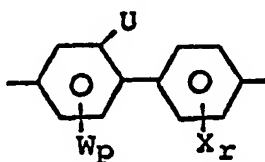
30 hydrogen.

9. A device according to claim 8 wherein each of said U and X substituents is selected from the group consisting of halogen, nitro, alkoxy and substituted-alkyl.

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10. A device according to claims 6 to 9 wherein each of said A and B radicals of said recurring units is said divalent radical (1).

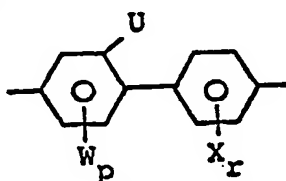
11. A device according to claim 10 wherein said divalent radical A is a radical having the formula (1).



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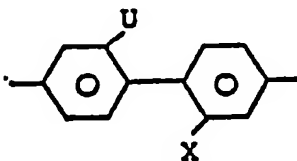
wherein p is the integer 3, r is the integer 4 and each of U, W and X is a substituent other than hydrogen, preferably a halogen such as fluoro.

12. A device according to claim 10 wherein said divalent radical A is a radical having the formula



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wherein p is the integer 3, r is the integer 4 and each of U, W and X is a substituent other than hydrogen; and said divalent radical B is a radical having the formula



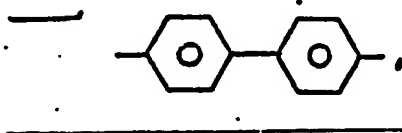
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wherein each of U and X is a substituent other than hydrogen.

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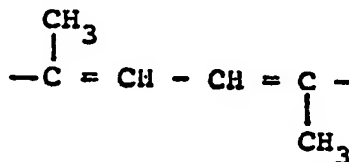


- 1 13. A device according to claims 6 or 7 wherein said di-  
valent radical A is the radical having the formula

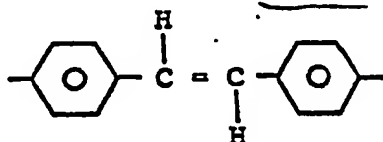


14. A device according to claim 7 wherein said B repre-  
sents a single bond.

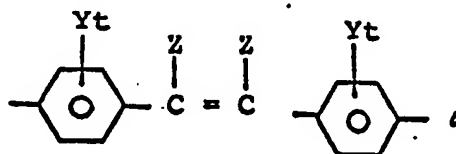
- 10 15. A device according to claim 7 wherein said divalent  
radical A is the radical having the formula



16. The device of claim 7 wherein said divalent radical A  
is the radical having the formula



- 25 17. A device according to claim 7 wherein at  
least one of said A and B radicals is said divalent radical  
having the formula



- 35 18. A device according to claim 17 wherein, Z is hydrogen,  
and t is the integer one.

1 19. A device according to claim 18 wherein said Y substituent is selected from the group consisting of halogen, nitro and alkoxy.

20. A device according to claim 17 wherein each Y is  
5 hydrogen, each t is the integer four, one said Z is hydrogen and the remaining said Z substituent is halogen.

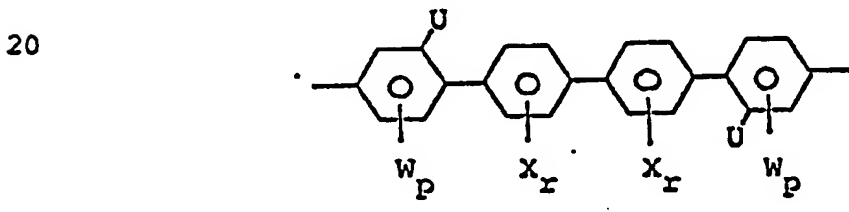
21. A device according to claim 6 wherein c is zero.

10 22. A device according to claim 7 wherein said divalent radical A is the radical having the formula



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said divalent radical B is a substituted-quaterphenylene radical having the formula



25 wherein each U is a substituent other than hydrogen, each W is hydrogen or a substituent other than hydrogen, each p is an integer from 1 to 3, each X is hydrogen or a substituent other than hydrogen and each r is an integer from 1 to 4, said U, W<sub>p</sub> and X<sub>r</sub> substitution being sufficient to  
30 provide said radical with a non-coplanar molecular configuration.

23. A device according to claim 7 wherein said divalent radical A is the radical having the formula

35

1 ation of bond and group polarizabilities of a repeating unit  
 of a polymer. It will be appreciated that electron density  
 distribution about axis X will be variously treated as a  
 cylindrical or ellipsoidal distribution depending upon the  
 relative magnitudes of the Y and Z vectors. In Fig. 4a is  
 5 shown an ellipsoidal cross-section along the axis of Fig. 3  
 where the magnitude of the shown Y vector is greater than  
 that of the Z vector. Ideally, Y and Z vectors would be  
 equal and the resulting circular cross-sectional distribut-  
 ion along the X axis is shown in Fig. 4b.

10

By a combination of longitudinal eccentricity ( $e_L$ ) and  
 transverse eccentricity ( $e_T$ ), based upon bond and group  
 polarizabilities, and the length and mean diameter of a  
 repeating unit, a geometric index, G, related to optical  
 15 anisotropy or birefringence, can be represented as follows:

$$G = 0.222 \left( \frac{1 + e_L}{1 + e_T} \right) \frac{L}{D}$$

20

wherein  $e_L$ ,  $e_T$ , L and D have the meanings hereinbefore  
 ascribed. Longitudinal eccentricity  $e_L$  may be represented  
 according to the following relationship

25

$$e_L = \frac{\sqrt{x^2 - \frac{(y^2 + z^2)}{2}}}{x}$$

Transverse eccentricity  $e_T$  may be represented by the  
 30 relationship

$$e_T = \frac{\sqrt{y^2 - z^2}}{y}$$

35

1 wherein the magnitude of vector Y is the larger of the Y  
and Z vectors. Ideally, transverse eccentricity  $e_T$  will  
equal zero and longitudinal eccentricity  $e_L$  will equal one,  
in which case, eccentricity factor, E, will equal the  
theoretical maximum of two.

5 Geometric index G can be calculated for a variety of re-  
peating units of a polymer material by resort to mean  
diameter and length values and longitudinal and transverse  
eccentricity values calculated from experimentally determined  
10 dihedral angles. It will be appreciated that the magnitude  
of values of length, mean diameter, longitudinal eccentricity  
and transverse eccentricity will materially influence the  
value of geometric index G. Thus, it will be appreciated  
that a repeating unit having, for example, a length of  
15 about twice that of a repeating unit having a different  
molecular structure and configuration will have a geometric  
index of about twice that of such different repeating unit.  
Accordingly, in making comparisons of geometric indices and  
magnitude thereof in relation to structural differences  
20 between comparative molecular repeating units, such differ-  
ences in length should be borne in mind.

In general, experimentally determined values of birefringence  
for polymeric materials comprised of repeating units as  
25 aforescribed will correlate directionally with values of  
geometric index, G, of the repeating units. Thus, in general,  
recurring units having higher geometric index values provide  
polymers exhibiting higher birefringence. Polymeric materials  
comprised of repeating units having a geometric index value,  
30 G, of about 0.5 or higher exhibit high birefringence and can  
be utilized in the optical devices of the present invention.  
It will be preferred, however, that polymeric materials  
comprising repeating units having geometric index values of  
one or higher be utilized herein. Especially preferred  
35 herein are polymers comprising repeating units of geometric

1 transparent layers, each said additional transparent layer  
having an index of refraction substantially matching one  
of the two indices of refraction of each said layer of  
said molecularly oriented highly birefringent polymer.

5 30. A multilayer device according to claim 29 wherein  
each said additional transparent layer is isotropic.

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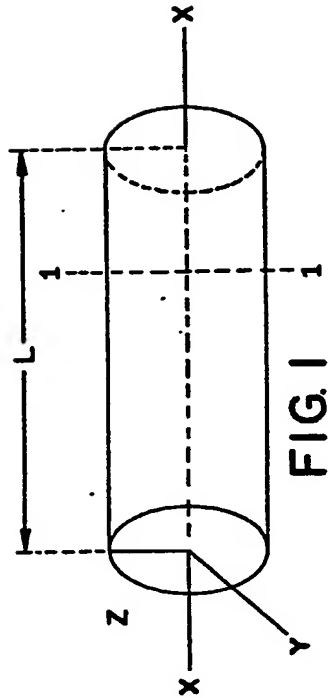


FIG. 1

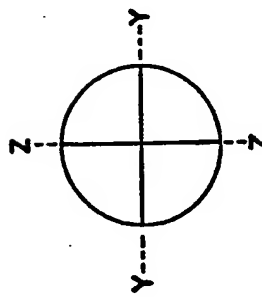


FIG. 2

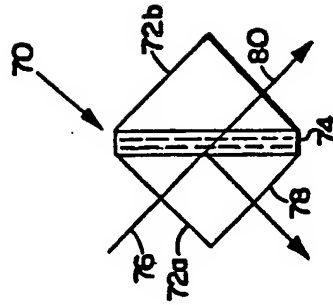


FIG. 8

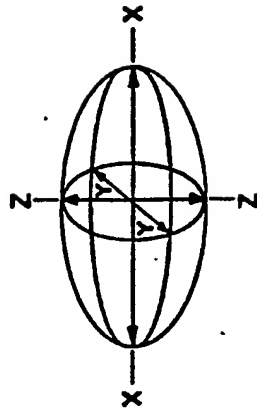


FIG. 3

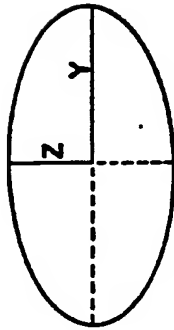


FIG. 4a

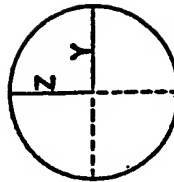


FIG. 4b

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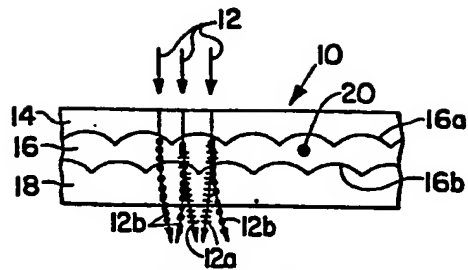


FIG. 5

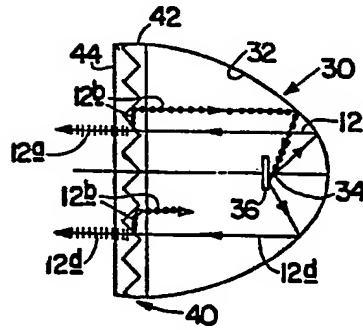


FIG. 6

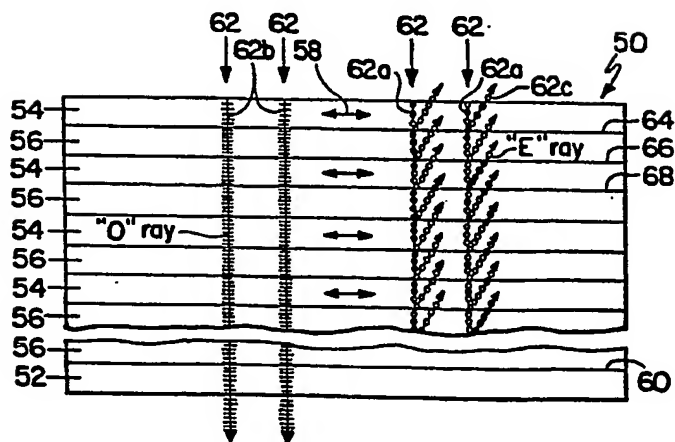


FIG. 7



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# EUROPEAN SEARCH REPORT

0062751

Application number

EP 82 10 1572.4

DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int. Cl. 3)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
Y	<u>US - A - 2 451 695 (R.S. SCHREIBER)</u> * claims 1, 5 to 7 * ---	1,6	G 02 B 1/08 C 08 G 69/32
Y	<u>GB - A - 1 011 836 (INTERNATIONAL POLAROID CORP.)</u> * claims 1, 7, 9 * ---	1,6	
A	<u>US - A - 3 801 528 (P.W. MORGAN)</u> * claims; column 4, lines 35, 36 * ---	6,17	TECHNICAL FIELDS SEARCHED (Int.Cl. 3)
A	Chemical Abstracts vol. 88 no. 4 23 January 1978 Columbus, Ohio, USA A.V. SIDOROVICH et al. "Quasicrystalline state of aromatic heterocyclic polymers with imide rings" page 9, column 2, abstract no. 23545n & Dokl. Akad. Nauk.SSSR vol. 237, no. 1 1977, pages 156 to 159 ---		C 08 G 69/00 G 02 B 1/08 G 02 B 5/30
D,Y	<u>US - A - 3 610 729 (H.G. ROGERS)</u> * claim 1; column 2, lines 50 to 65; fig. * ---	1,5, 29,30	CATEGORY OF CITED DOCUMENTS
D,Y	<u>US - A - 3 522 984 (H.G. ROGERS)</u> * column 3, lines 62 to 74 * ---	1,5	X: particularly relevant if taken alone Y: particularly relevant if combined with another document of the same category A: technological background O: non-written disclosure P: intermediate document T: theory or principle underlying the invention E: earlier patent document, but published on, or after the filing date D: document cited in the application L: document cited for other reasons
<input checked="" type="checkbox"/> The present search report has been drawn up for all claims			&: member of the same patent family, corresponding document
Place of search		Date of completion of the search	Examiner
Berlin		11-05-1982	HASS/FUCHS



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Application number

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DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int. Cl.)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
D,Y	<u>US - A - 3 213 753 (H.G. ROGERS)</u> * column 3, lines 8 to 28; column 9, line 74 to column 10, line 14 * ---	25-28	
A	<u>DE - C - 732 790 (H. SCHNEIDER AG)</u> * claim 1 * ---	1,5	
A	<u>US - A - 2 748 659 (W. GEFFCKEN et al.)</u> * fig. 1 * ---		
			TECHNICAL FIELDS SEARCHED (Int. Cl.)